Materials Research Express

PAPER

Evolution of spectroscopy features in layered MoS_xSe_(2-x) solid solutions

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Keywords: transition metal dichalcogenides, MoS_xSe_(2-x), Raman spectroscopy

Supplementary material for this article is available online

Abstract

In this work we report the structural and spectroscopic characterization of the bulk MoS_xSe_(2-x) solid solutions synthesized by chemical vapor transport. The bulk crystals were analyzed by scanning electron microscopy (SEM), x-ray diffraction (XRD), energy dispersive spectroscopy (EDS), atomic force microscopy (AFM), x-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. Electron microscopy evaluation of the layered materials shows two distinct types of crystals: flat and easily cleavable hexagonal microcrystals up to 50 μm in size, and agglomerated irregular crystals of 5–10 μm in size. XRD shows a consistent increase in interplanar spacing as the Se content is increased in the sample series. Raman spectra of bulk MoS_xSe_(2-x) obtained with three different excitation energies revealed first order phonon modes associated with pure MoS_2 (x = 2) and MoSe_2 (x = 0) along with a complex behavior of vibrational modes when x had intermediate values. XPS Mo_3d line scans indicate a slight shift towards lower binding energies as the Se/S ratio increases, consistent with the expected energies of MoSe_2. A simple and direct relationship can be established between the characteristic Raman peaks and the value of x, which can be useful for identifying the compositions of TMD crystals.

1. Introduction

Semiconducting transition metal dichalcogenides (TMDs) MX_2 systems, where M is a transition metal atom (Mo, W) and X is a chalcogen atom (S, Se), exhibit a unique combination of thickness dependent bandgap and strong spin–orbit coupling, resulting in favorable electronic, optoelectronic and mechanical properties [1, 2]. The layers composing a bulk TMD crystal, can also be isolated, and a single layered TMD, such as MoS_2, becomes a direct band gap semiconductor, in contrast with bulk crystals, which have an indirect band gap [3, 4]. Additionally, their band gap can also be tuned upon changing their chemical compositions [5, 6]. TMDs have been the subjects of an important research field as they offer the possibility of combining different atomically thin layers and build artificial van der Waals solids [7]. Composite materials in combination with TMDs have been proposed for medical applications, catalysts for water splitting [8, 9], detection of NO_2 [10], and, in
combination with oxygen and nitrogen, for fungicide applications [11]. S-based TMDs are strong candidates to join the technology race for photodetector arrays for machine vision systems [12] and memristive devices for neuromorphic applications [13].

Theoretical and experimental efforts have focused on the behavior of semiconducting MX₂ in monolayer and bilayer forms, with particular interest in their distinctive photoluminescence emission [3, 4, 14, 15], as well as the importance of the crystalline defects like ion intercalation [16], chalcogen and metal substitution [14, 17, 18]. For example, the role of thermal phonons in Mo₁₋ₓWₓS₂ embedded in WS₂ nanoscale domains reported by Gu et al [19], show that collective scattering mechanisms produce lower thermal conductivity in Mo-W alloys when compared to that of pristine MoS₂ crystals. Regarding their synthesis, scalable grain size of MoS₂ monolayers reported by Zhang et al [20] indicate that in monolayered crystals the grains can have a wide range of sizes, from 20 nm up to 1 μm. A variety of different substrates for CVD growth of TMDs is also possible, widening the possibilities for improving device applications and performance [21].

CVD techniques for the growth of monolayer MX₂-type structures have seen a huge progress in the last few years and show remarkable results [21–23]. For example, a simple method to synthesize Mo-W alloys, triangular monolayers [24] with a wide range of stoichiometry morphologies has been achieved by varying CVD conditions, like the introduction of Se together with S during the growth to produce changes in the bandgap of the monolayers [25–28] and photoluminescence (PL) emission. Another technique utilizes a pre-seeding strategy, where tungsten oxide nanoparticles are used to coat the substrate surface in order to get a uniform single layer growth [8]. However, bulk crystal growth of layered semiconductors has an accumulated knowledge of several decades [2, 29, 30]. The outstanding crystalline quality of bulk TMDs, subsequently thinned by mechanical exfoliation facilitated the first studies of the optical and electronic properties of MoS₂ monolayers [4]. Nowadays mechanically thinned CVT grown crystals continue to have potential for probing the properties of new layered materials [31, 32].

For both bulk and monolayer crystals, the simultaneous incorporation of chalcogen atoms like Se and S, or transition metal atoms like W and Mo, have a definitive impact on the morphology and electronic properties. It is precisely the stoichiometric ratios that determine the vibrational behavior of the layers and whose normal modes of vibration are perceptible using spectroscopic techniques [27, 33–36]. In this work, we study spectroscopic features of MoₓSe₁₋ₓ bulk crystals. The solid solutions have been grown by a reliable solid-state method of vibration are perceptible using spectroscopic techniques

2. Methods

The MoSₓSe₂₋ₓ crystals were grown by chemical vapor transport (CVT) in a two-step process previously described by Nguyen et al [6]. The various percentage series was synthesized for 0 ≤ x ≤ 2 in x = 0.2 steps with an initial corresponding stoichiometric mixture of molybdenum powder (Acros Organics 99.9%), sublimated sulfur powder (J.T. Baker), and selenium powder (Acros Organics 99.5+ %) placed in a vacuum sealed ampoule and heated in a tube furnace at 1000 °C for 3 days. For the second growth step by CVT, the obtained solid solution powders of MoₓSe₂₋ₓ were placed in an ampule together with iodine as the transport gas and then heated in a two-zone furnace at 950 °C and 870 °C, for the source and growth zones, respectively. A schematic view of the CVT method is shown in figure 1. The layered crystals were then washed using hexane and dried under vacuum to remove solvent and residual iodine. CVT growth yields larger crystals with high quality suitable for mechanical cleavage and exfoliation for AFM characterization, while preserving the stoichiometry of the first growth step [6]. While CVT presents equilibrium conditions for solid state reactions.

For EDS and XPS characterization, samples were evenly distributed onto a double-sided carbon tape forming a continuous layer of bulk crystals. For Raman and AFM characterization, crystals were mechanically exfoliated to obtain thinner layers and transferred to a 300 nm SiO₂/Si substrate.

SEM images were used to determine the morphology and size of the bulk samples. For samples of x composition between 0.6 and 1.4, a JEOL JIB-4500 was used, and for the rest of the samples, a Zeiss Field Emission SEM Supra 55 VP. The microscopes were operating at 13 and 5 kV, respectively. For EDS and elemental mapping, an Oxford X-Max analyzer equipped with an X-Max silicon drift detector (20 mm²) and the INCA X-Stream 2 and MICS software (Oxford Instruments) was used. The atomic percentage uncertainty of the detected elements corresponded to the standard deviation (sigma) of the INCA software calculation operated with a standards-based sequence.

For a qualitative comparison of MoₓSe₂₋ₓ crystals of different compositions, we acquired XPS spectra, using an x-ray photoelectron spectrometer PHOIBOS WAL equipped with a monochromatic Al Kα radiation
(1486.6 eV) light source (SPECS). Charge effects in the XPS spectra were corrected using the value of the binding energy of carbon 1 s peak at 284.8 eV as reference.

For surface imaging and characterization, AFM operated in contact mode (c-AFM) at room temperature (Park Systems XE-70) was used on crystals transferred onto silicon substrates. XRD measurements were performed on a PANalytical X’Pert Pro multipurpose x-ray diffractometer equipped with a Cu Kα source.

The Raman measurements were performed in a Horiba T64000 and a Horiba LabRAM spectrometers. The Horiba T64000 System was equipped with a liquid nitrogen-cooled CCD and the LabRAM was equipped with a Peltier-cooled CCD. The Horiba T6400 was used with a 514 nm laser wavelength, and a grating with 600 lines mm⁻¹, while the LabRAM was used with both 633 and 473 nm lasers and an 1800 lines mm⁻¹ grating. The power was kept at or below 1 mW to avoid unnecessary heating/burning of the samples.

3. Results and discussion

SEM micrographs in figure 2 depict two distinctively different morphologies: grains formed by a collection of smaller crystals (stacked) along its planar direction (type A) as shown in figure 2(a) and flat hexagonal and considerably larger crystals figure 2(b) with well-defined facets (type B). The SEM images for the other compositions can be observed in figure S1 (available online at stacks.iop.org/MRX/9/046301/mmedia) in the supporting information. The observed difference in morphology may be attributed to the presence of stacking faults along the crystallographic c-axis, which was demonstrated to be most prevalent in sulfur-rich compositions, most probably due to the difference in atomic radii between S and Se⁴.
Figure 3. (a) XRD spectra for most of the samples of the MoS$_x$Se$_{2-x}$ series. All peaks show a noticeable shift towards lower diffraction angles (higher interplanar spacing) as Se content increases. (b) A detailed view of the (006) diffraction peaks. Spectra intensities where normalized to the (002) MoS$_2$ peak and shifted vertically for clarity. (c) Measured changes in interplanar spacing for three different atomic planes as a function of Se content. An average of 5% total increment in interplanar spacing is observed from $x = 2$ (MoS$_2$) to $x = 0$ (MoSe$_2$).
behavior of the spacing. This is to be expected, as the Se ion is larger than the S ion by 17%. Figure 3
substrate for AFM characterization. Figure 5
other samples of different S
levels show an approximate crystal thickness of 500 nm
flakes of incomplete layers. Topographical line scans in d,
ake obtained from the AFM topography scan, a closer inspection of the surface
planes, which is of the same order of magnitude as the difference in the crystallographic parameters of the
hexagonal structure of the two extreme-end solid solutions MoS2
approximately 4%. from ICSD, reference code 00
EDS analysis was carried out on the bulk samples to determine the S
EDS spectra and the elemental maps of Mo, S, and Se of the MoSxSe2-x, samples estimated from the EDS spectra for each concentration.

In figure 3 we show the XRD data for most of the samples in the series, with intensities normalized to the (002) MoS2 peak and an arbitrary offset added in the vertical direction for clarity. A clear shift of all peaks towards lower diffraction angles is observed as the Se content is increased, implying an increase in interplanar spacing. This is to be expected, as the Se ion is larger than the S ion by 17%. Figure 3(b) shows a more detailed behavior of the (006) peak for increasing Se content in the MoSxSe2-x solid solution. In order to estimate this expansion, the relative increase in interplanar spacing was calculated using the XRD data for the (002), (006) and (008) peaks as a function of Se content. Figure 3(c) shows the total increase to be between 5 to 6% for these planes, which is of the same order of magnitude as the difference in the crystallographic parameters of the two extreme-end solid solutions MoS2 (a = 3.161 Å) and MoSe2 (a = 3.287 Å) of approximately 4%, from ICSD, reference code 00–029–0914; 00–037–1492.

EDS analysis was carried out on the bulk samples to determine the S/Se ratio. Figure 4 shows the results of atomic concentration measurements and elemental mappings of the samples as obtained by EDS. Figures 4(b), (d) and (e) show the elemental mappings for Se, S and Mo respectively of a small MoS0.2Se1.8 crystal transferred to a SiO2/Si substrate. A uniform distribution of the atomic components is clearly observed for this crystal, as for other samples of different S/Se ratios. The experimentally determined chalcogen concentrations (figure 4(f)) is in good agreement with the initial quantities of each chalcogen that were used during the first growth step as previously reported.

For a closer inspection of the surface morphology, MoS1.4Se0.6 crystals were transferred onto a silicon substrate for AFM characterization. Figure 5(a) shows an optical microscopy image of a ~20 μm crystal with a fairly flat surface, an ideal morphology for mechanical exfoliation. Figure 5(b) shows the three-dimensional rendering of the flake obtained from the AFM topography scan, a closer inspection of the surface (figure 5(c)) reveals smaller flakes of incomplete layers. Topographical line scans in d) of the edge of the crystal and of the top layers show an approximate crystal thickness of 500 nm (~ 400 monolayers), and 80 nm respectively.

XPS analysis was also performed on our series of samples, focusing on the 3d molybdenum peaks, and a weak 2 s sulfur peak centered at ~227 eV, as shown in figure 6. The Mo-3d3/2 and 3d5/2 peaks centered at ~233 eV and ~230 eV, respectively for MoS2 (x = 2), shift ~ 0.5 eV towards lower binding energies, and the sulfur 2 s peak decreases in intensity as x → 0 (MoSe2), consistent with our EDS findings presented in figure 4. The energies of these XPS peaks correspond to the 2H phase of MoS2 and MoSe2 for the extreme-end cases (x = 2 and x = 0), as well as other S and Se peaks shown in figures 6(b) and (c). figures 6(b)) shows the 3d photoelectron spectra for selenium, which actually consists of two peaks, centered around 55.6 eV and 54.7 eV, corresponding to Se-3d3/2 and Se-3d5/2, respectively. The intensity of these peaks increases according to the Se content in the samples, starting from no-selenium in MoS2. The XPS curves in figure 6(c) show a more complex behavior, with contributions from the S-2p peaks as well as Se-3p single peak. For MoS2 (x = 2), the S-2p1/2 (163.2 eV) and S-2p3/2 (162.3 eV) form the main peak, but as the Se content increases, the Se-3p3/2 peak becomes a noticeable shoulder around 161 eV for x = 1.2, that dominates the spectrum as Se content increases while the S-2p peaks disappear.

Raman spectroscopy was used to characterize the bulk vibrational modes and their relation with the S-Se content. For bulk TMDs, two set of vibrations are predominant; the out-plane vibration mode, designated as the
A$_{1g}$ mode, and the in-plane vibration mode or E$_{2g}$ mode. Figures 7(a)–(c) show a series of Raman spectra acquired with 1.96, 2.41 and 2.62 eV lasers for the MoS$_x$Se$_{2-x}$ samples. At $x = 2$, corresponding to pure MoS$_2$, the curves show the characteristic E$_{2g}$ peak at ~380 cm$^{-1}$ and the A$_{1g}$ peak at ~410 cm$^{-1}$, while at $x = 0$, corresponding to pure MoSe$_2$, the A$_{1g}$ peak at ~240 cm$^{-1}$ and the E$_{2g}$ mode at ~285 cm$^{-1}$ are clearly visible. The broad band at ~465 cm$^{-1}$ in figure 7(a) for $x = 2$, corresponds to a combination of LA phonons in MoS$_2$, which
is enhanced due to the resonance with the excitons [37]. At $x = 0$, in figures (b) and (c), another band can be observed at $\sim 440$ cm$^{-1}$, corresponding to combinations of phonons in MoSe$_2$, which is also enhanced for laser energies near the C exciton [38]. The resonance Raman processes related to the pure MoS$_2$ and MoSe$_2$ crystals are intrinsically connected to their electronic structure [37, 39] and can be strongly affected by the changes induced by the composition of the solid solutions.

For intermediate values of $x$, the Raman spectra has a more complex behavior. As the Se content increases ($x \rightarrow 0$) the MoS$_2$-like peaks shift to lower frequencies. As the Se/S ratio increases, the crystalline structure changes since the bond lengths of Mo–S and Mo–Se are different, thus affecting the vibration modes. Similar Raman behavior has been reported for ternary alloys Mo$_{(1-x)}$W$_x$S$_2$, where the transition metal composition is gradually changed [40]. In this study, the broad peak attributed to MoSe$_2$ at $\sim 440$ cm$^{-1}$ is detectable at the extreme compositions closer to $x = 0$, meanwhile, the broad peak at $\sim 465$ cm$^{-1}$ attributed to MoS$_2$ appears closer to $x = 2$, and both peaks vanish for $1.4 > x > 0.6$. The 465 cm$^{-1}$ peak is more significantly affected with the 1.96 eV laser, and it sharply decays in intensity from $x = 2$ to $x = 1.8$.

In figure 7, it becomes apparent that the resonance with the A and C excitons is extremely relevant to the intensity of the zone-center phonons in pure MoS$_2$ [41]. In figure 7(a), in the range $1.8 > x > 0.4$, the intensity of the MoS$_2$-A$_{1g}$-like phonon is enhanced, in particular close to $x = 2$. The enhancement can be attributed to a resonance with the A exciton, which gets closer to the laser energy at $x = 1.8$ [6, 40]. The same reasoning can be applied to the other lasers, when we consider the resonance with the C exciton. In fact, given that the C excitons of bulk MoSe$_2$ is at a lower energy than bulk MoS$_2$, using a laser in resonance with the C excitons of MoS$_2$ will leave the MoSe$_2$ sample completely out of resonance. This behavior carries over to the range $1.8 > x > 0.4$, where we can observe the intensity of the MoS$_2$-like A$_{1g}$ and E$_{2g}$ peaks increasing in intensity as $x$ increases.

Another interesting feature is the appearance of a pair of peaks at $\sim 225$ and $255$ cm$^{-1}$ that become noticeable beginning at $x \sim 0.2$, and shift to higher and lower frequencies, respectively, as the Se content increases. These two peaks appear to merge towards the A$_{1g}$ mode of MoSe$_2$. A similar shifting of the A$_{1g}$ mode, along with second peak at higher frequencies have been reported by Mahjouri-Samani et al [42]. In that study, the authors conducted computational simulations to explain the experimentally observed new peak at $\sim 250$ cm$^{-1}$. Such defect-driven peak, which was directly associated with a material with a high density of selenium vacancies, softens when the concentration of defects decreases. The A$_{1g}$ mode, on the contrary, softens when the concentration of selenium vacancies increases, which is consistent with the behavior that we observe in our experimental data. Therefore, there is a possibility that such defect-driven peak can also be associated with a high density of sulfur atoms replacing selenium atoms.
4. Conclusions

We have shown that the CVT method is a reliable synthesis method for the growth of MoS\textsubscript{x}Se\textsubscript{2-x} bulk crystals, owing to its near-equilibrium growth parameters. The EDS results show that this technique allows for an excellent control of the Se/S content in the MoS\textsubscript{x}Se\textsubscript{2-x} solid solutions, as the concentration ratio of both chalcogens in the first growth step matches the one determined by EDS. EDS mapping shows no evidence of phase separation, quite the contrary, we observed homogeneous solid solutions of the bulk crystals. Diffraction data shows a monotonic increase in interplanar atomic spacing of the structural lattice as the Se/S ratio increases.

XPS line scans of the Mo-3p\textsubscript{3/2} and 3p\textsubscript{1/2} peaks show a clear and gradual shift towards lower binding energies as x \to 0 (increasing Se content), ending with binding energies corresponding to pure MoSe\textsubscript{2}. The gradual change of the Se/S ratio in the samples is also reflected in the observed complex behavior of the Raman spectra, with the active modes at the extreme compositional points (x = 0, x = 2) corresponding to pure MoSe\textsubscript{2} and MoS\textsubscript{2}. Intensity variations of the Raman peaks upon changes in the laser energy have been attributed to resonance effects. Therefore, EDS, XRD and XPS studies have enabled the identification of Raman signatures associated with all the studied solid solutions, thus allowing the optical identification of a given S-Se composition based solely on Raman spectroscopy.

Acknowledgments

The SEM work was partially funded by A L E’s Grant from Analytical and Diagnostics Laboratory (ADL) at Binghamton University. The authors AFP and JVB would like to thank E Aparicio, E Murillo, I Gradilla and D Domínguez, for their valuable support with XRD, AFM, SEM and XPS analysis. This work was partially funded by DGAPA-PAPIIT, grant No. IN115420. AFP also acknowledges the financial support of CONACyT-Mexico scholarship program.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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