



Molybdenum diselenide formation using electrochemical atomic layer deposition (E-ALD)



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ARTICLE INFO

Article history:

Received 21 November 2016

Received in revised form 25 January 2017

Accepted 31 January 2017

Available online 3 February 2017

Keywords:

Electrochemical Atomic Layer Deposition (E-ALD)

Molybdenum diselenide thin films

Underpotential deposition

Molybdenum electrodeposition

Selenium electrodeposition

Cyclic voltammetry

ABSTRACT

Cyclic voltammetry (CV) of Au in MoO_3 and SeO_2 solutions was studied under both basic and acidic conditions, as a precursor to development of E-ALD cycle chemistry for the electrodeposition of MoSe_2 . Those results indicated that acidic HMoO_4^- and SeO_2 precursor solutions would be a better choice for the formation of MoSe_2 using E-ALD. Photoelectrochemical (PEC) photovoltage measurements revealed an optical band gap of 1.1 eV for the as-deposited MoSe_2 films. Some unreacted MoO_2 was detected by the PEC measurements, as well, but were removed by thermal annealing. Some excess elemental Se was also removed during the anneal, and Raman spectroscopy indicated that the films' crystallinity was improved. Deposit quality was followed using X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and electron probe microanalysis (EPMA). Se appeared to suppress Mo oxidation and induce MoSe_2 film growth in the E-ALD cycle.

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1. Introduction

Graphene is the epitome of a 2-dimensional (2D) material and has garnered great attention recently [1]. Another category of 2D materials is the transition metal dichalcogenides (TMDC), which are becoming increasingly important to material chemists, physicists, and engineers. TMDCs have the general formula MX_2 , where M is a transition metal (such as Ta, Nb, Mo, or W) and X is a chalcogen (S, Se, or Te) [2]. Each layer of MX_2 is a trilayer, made up of a sandwich of two chalcogen layers on either side of a transition metal center layer. The trilayers are held together via van der Waals interactions in the bulk material, and different structural polytypes exist depending on the stacking sequence [3].

TMDCs exhibit numerous intriguing properties, suggesting a wide range of potential applications. One such property is the ability of some TMDC to undergo Peierls transitions to form charge density waves (CDW) [4]. The possibility of utilizing CDW in electronic device applications has been considered, stimulating a desire to try and grow TMDC nanofilms layer-by-layer with an alternative growth method [5,6]. Preliminary electrodeposition studies of chalcogens

onto Ta substrates by this group yielded promising results, affirming electrodeposition as a viable option for growing TMDC [7].

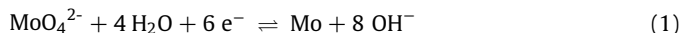
In the study presented here, Electrochemical Atomic Layer Deposition (E-ALD) was used to grow molybdenum diselenide (MoSe_2). Whereas conventional ALD is based on the use of gas-phase surface limited reactions, E-ALD is based on the use of electrochemical surface-limited reactions to deposit thin films. Electrochemical surface-limited reactions are generally referred to as underpotential deposition (UPD) [8–14]. In E-ALD, atomic layers of the desired elements are alternately deposited on each other, in a cycle, with the number of cycles performed dictating deposit thickness.

Properties of molybdenum dichalcogenides have been widely investigated for their potential applications. As the material thickness decreases, band gaps of MoS_2 and MoSe_2 exhibit a crossover from indirect to direct transitions in the limit of a single layer [15–17]. Owing to their band gap energies in the UV-visible region, MoS_2 and MoSe_2 have potential uses in photonics and optoelectronics [18,19]. In the area of renewable solar energy research, MoSe_2 has been used as a catalyst for the hydrogen evolution reaction (HER) [20,21]. Group 6 transition metal dichalcogenides, such as MoSe_2 and MoS_2 , are well-suited as photoelectrodes in regenerative electrochemical solar cells because they are less susceptible to photodecomposition. Their photogenerated excitons originate from the non-bonding *d*-orbitals, thus the photo-initiated reactions arising from these transitions do not directly result in bond breaking [22].

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The difficulty in electrodepositing MoSe₂ stems from the negative standard potential for molybdenum, indicating that the HER should thermodynamically occur as well. In theory, Mo electrodeposition can proceed by the following reaction [23,24]



E^0 for the reaction is -0.913 V vs. SHE. Mo electrodeposition from an aqueous solution typically exhibits only $\sim 1\%$ current efficiency, at best, due to the concurrent HER, the dominant side reaction [25,26]. Metallic Mo is more easily electrodeposited as an alloy with Fe, Co, or Ni [27,28]. If Mo is more successfully co-deposited, it might be that Se could help induce Mo electrodeposition [29–32]. The work presented here examines the electrodeposition of Mo in the presence of Se to form MoSe₂.

2. Experimental

All potentials are reported vs. an Ag/AgCl (3 M KCl) reference electrode (Bioanalytical Systems, Inc.). The Au substrates (EMF Corp) were 100 nm of Au (99.9%) evaporated onto glass slides coated with 5 nm of Ti as an adhesion layer. All solutions were prepared with 18 M Ω H₂O from a Milli-Q purification system. The MoO₃ solutions were prepared by sonicating, to dissolve the MoO₃ (J.T. Baker, 99.5%) powder, with one NaOH pellet (Fisher Scientific, 99.6%) in $\sim 20 \text{ mL}$ H₂O. The solution was then diluted to its final volume, and the pH was adjusted. The basic MoO₃ solution (pH 8.3) was prepared by addition of NH₄Cl (Macron Fine Chemicals, ACS grade) prior to dilution. The acidic HMoO₄[−] solution (pH 1.5) was prepared by addition of HClO₄ (J.T. Baker, 60–62%) to the dissolved MoO₃; no NH₄Cl was added. The SeO₂ (Alfa Aesar, 99.999%) solutions were prepared by dissolution in H₂O, and adjustment of the pH with HClO₄ or NaOH. All solutions contained 0.1 M NaClO₄ as a supporting electrolyte. The NaClO₄ stock solution was prepared by neutralizing HClO₄ with NaOH. MoSe₂ powder (99.9%), purchased from Alfa Aesar, was used as a reference for Raman studies.

All electrochemical experiments were performed using an automated flow cell deposition system (Electrochemical ALD, L.C., Athens, GA). The system was composed of solution bottles, connected through Teflon tubes to a solenoid activated Teflon distribution valve. The valve was connected to the electrochemical flow cell, from which solutions flowed through a peristaltic pump to waste. The cell was operated in the 3-electrode mode, with the Au on glass slides, noted above, used as the working electrodes, the 3 M Ag/AgCl reference electrode, and an Au wire inlaid into the cell wall, across from and parallel to the planar working electrode, used as the auxiliary electrode. The cell volume was about 0.3 mL, and the exposed electrode area was 0.7 cm². The whole system was interfaced to a computer to allow remote control of the potentiostat, cell potential, solutions, and flow time. The LabVIEW-based system control software was written in-house. During MoSe₂ deposition, the flow rate was maintained at 15 mL min^{−1} for all flow steps in the cycle. CVs were performed at 10 mV s^{−1}, with the solution flowing at $\sim 2 \text{ mL min}^{-1}$. All solutions were deaerated by purging with N₂ (Airgas) prior to and during experiments.

Electron probe microanalysis (EPMA) was performed on a JEOL JXA-8600 Superprobe, using 10 μm electron beam diameter, 10 keV accelerating voltage, and 15 nA beam current. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were performed on a FEI Inspect F50 FEG SEM (FEI, Hillsboro, OR). STM images were obtained in air using a Nanoscope III (Digital Instruments, Santa Barbara, CA) with a tungsten tip. Raman spectra were obtained using a Renishaw inVia Raman microprobe (Renishaw, Wotton-under-edge, U.K.) equipped with a CCD detector. A 514 nm Ar-ion laser (Modu-Laser, LLC, Centerville, UT) running

at 0.67 mW was used as the excitation source. An 1800 lines/mm grating and a 20X objective were used during the spectral acquisition. X-ray photoelectron spectroscopy (XPS) was performed using a Mg K $\alpha_{1,2}$ (STAI B) X-ray source, at $\sim 70^\circ$ to the hemispherical analyzer axis (Leybold Heraeus). The Au 4f_{7/2} peak at 84.0 eV originating from the substrate was used to calibrate binding energies. Shirley background corrections were applied for each spectrum [33].

Photoelectrochemical (PEC) measurements were performed using light from a 300 W Xe arc lamp (Oriel Instruments, Stratford, CT), dispersed with an Oriel Cornerstone 260 Model 74100 monochromator, equipped with a 1200 lines/mm grating. The light was then chopped at 20 Hz and illuminated onto the MoSe₂ sample through a quartz window. The sample was immersed in 0.1 M NaClO₄, pH 1.5. The photovoltage was measured as the 20-Hz component of the open-circuit potential, through a lock-in amplifier (Standard Research Systems Model SR830, Sunnyvale, CA).

Sample annealing was performed in a tube furnace (Lindberg/Blue Model TF55030A-1, Asheville, NC) in 1%/99% H₂/Ar (Airgas). The temperature was ramped from room temperature up to the annealing temperature at 5 $^\circ\text{C min}^{-1}$. After half an hour at the annealing temperature, it was ramped down to room temperature at no more than 5 $^\circ\text{C min}^{-1}$.

3. Results and discussion

3.1. Voltammetric behavior of Mo and Se

Fig. 1 is a cyclic voltammogram (CV) for Au in 1 mM MoO₃ and 1 M NH₄Cl (pH 8.3). The scan started negative from 0.06 V, the open-circuit potential (OCP), to -1 V . Reduction began abruptly near -0.85 V . The rapid increase in current at -0.85 V is consistent with the overpotential for the HER on Au. However, on the positive-going scan, the HER ceased near -0.75 V , which is more consistent with the overpotential for the HER on Mo [26]. Positive of -0.75 V , oxidative current was evident in two regions: a broad oxidation feature between -0.75 V and -0.27 V , followed by a Gaussian-shaped peak, at -0.18 V .

The CV of Au in an acidic HMoO₄[−] solution, pH 1.5, is displayed in Fig. 2. In the negative-going scan from the OCP, 0.42 V, a reductive shoulder was observed at -0.3 V , prior to the onset of HER. This current was attributed to reduction of Mo^{VI} species, probably HMoO₄[−]. At -0.4 V , current for the HER increased rapidly, though no hysteresis was observed in the subsequent positive-going scan, in contrast

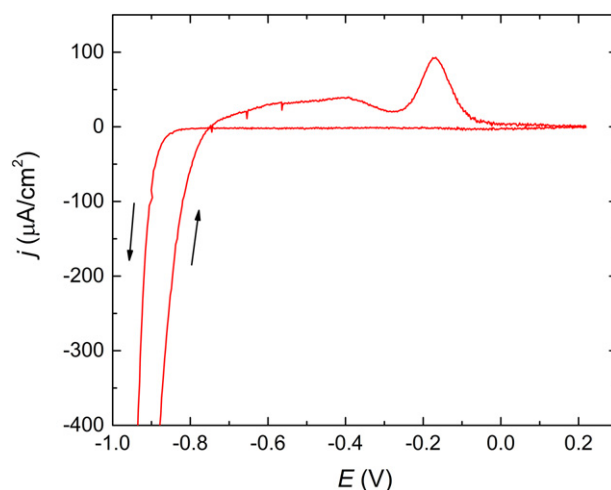


Fig. 1. CV of Au in a solution of 1 mM MoO₃, 1 M NH₄Cl, and 0.1 M NaClO₄ (pH 8.3). Open-circuit potential was 0.06 V. The initial sweep direction was negative from OCP, and the sweep was reversed at -1 V . A hysteresis loop was observed in the HER region, followed by two oxidative features.

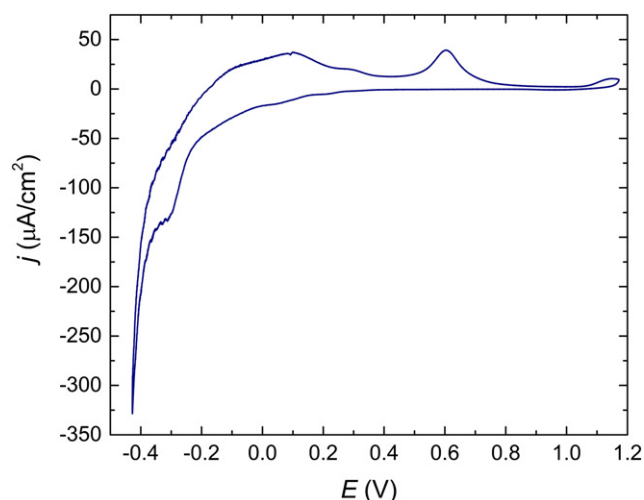


Fig. 2. CV of Au in 1 mM HMoO_4^- and 0.1 M NaClO_4 (pH 1.5). No NH_4Cl was added to the solution. The open-circuit potential was 0.42 V. The initial sweep was from OCP to -0.43 V. The oxidation features in the reversed sweep are similar to those observed in the pH 8.3 solution.

to Fig. 1 for the pH 8.3 solution. The oxidation features, however, were similar to those in Fig. 1: a broad oxidation, followed by a Gaussian-shaped peak.

For the sake of discussion, it is presumed that elemental Mo is deposited at low potentials; however, it is difficult to prove, under the characterization conditions, that some limited amount of a MoO_x species was not also present during deposition. Using the flow cell, Mo was deposited onto an Au electrode at -0.41 V for 30 s in the acidic HMoO_4^- solution. The solution was then replaced with blank at OCP (-0.18 V), and a CV was run with the solution flowing (Fig. 3). The CV started from OCP and scanned in the positive direction to 0.20 V. The broad oxidation was reminiscent of a passivation process [7,34]. After oxidation to 0.20 V, the potential sweep was reversed and scanned to -1.3 V, followed again by an oxidative sweep to 0.2 V

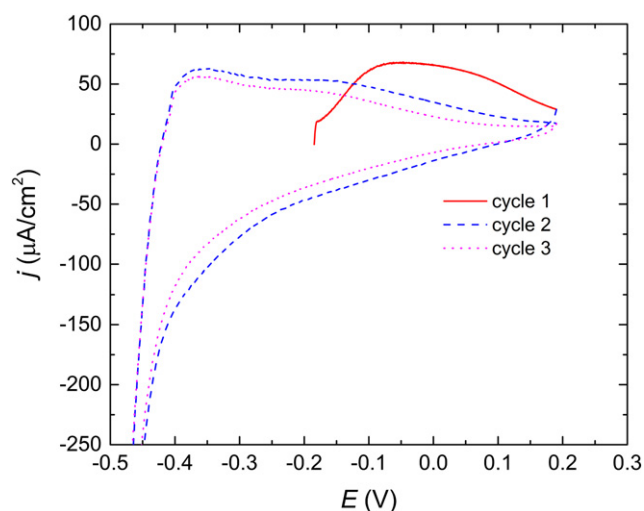


Fig. 3. CV of MoO_x/Au in 0.1 M NaClO_4 blank (pH 1.5). The MoO_x was deposited at -0.41 V for 30 s in the acidic HMoO_4^- solution. The open-circuit potential in blank was -0.18 V. In cycles 2 and 3, the negative-going sweep was reversed at -1.3 V. The subsequent broad oxidation feature would disappear if the potential were scanned to 1 V instead of 0.2 V. Cathodic current in the region negative of -0.5 V is not shown because that current was almost entirely associated with HER, with no distinguishable feature for MoO_x reduction.

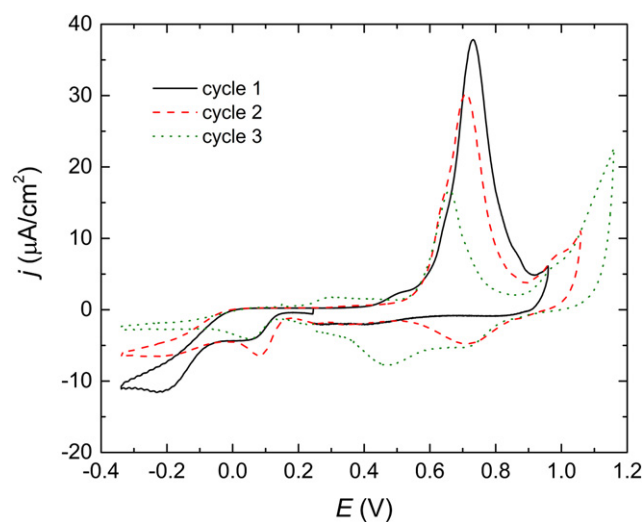


Fig. 4. CV of Au in 0.1 mM SeO_2 and 0.1 M NaClO_4 (pH 5). The open-circuit potential was 0.24 V, and the initial sweep was in the negative direction from the OCP. After scanning to -0.34 V, the subsequent oxidation (onset at 0.5 V) corresponded to no more than 0.5 monolayer of Se on Au.

(Fig. 3, cycle 2) in the blank. The reappearance of the broad oxidation feature in blank indicates that the product of the oxidation was insoluble, and remained on the surface, to be reduced again. On the other hand, by scanning to 1 V (not shown), the insoluble product of the oxidation was further oxidized and became soluble, and on the subsequent cycle the oxidation features, in Fig. 2, disappeared. The Pourbaix diagram suggests that reduction in an acidic HMoO_4^- solution would result in Mo deposition, and that oxidizing to 0.2 V should form solid MoO_2 , which is consistent with the results above [35]. Scanning to 1 V resulted in conversion of the insoluble MoO_2 to soluble HMoO_4^- , which was rinsed away by the blank. This dissolution coincides with the “Gaussian” oxidation feature at 0.6 V (Fig. 2). An in situ chemical or spectroscopic probe would be needed to establish the exact number and identities of the oxidized Mo species.

Selenium deposition was also examined as a function of pH. In pH 8.3, no Se deposition was evident in a CV of an Au electrode in 0.1 mM SeO_2 . At pH 5 (Fig. 4), Se deposition appeared to be limited to UPD. The onset of UPD oxidation (cycle 1) was 0.5 V, and resulted in an oxidation charge for Se stripping of around 0.5 monolayer (ML). A ML is defined in this report as one adsorbate (Se) for every substrate surface atom (Au). In pH 1.5, the Se deposition and stripping features (Fig. 5) shift positively. On the negative-going scan, from the OCP (0.43 V), the first two reduction peaks correspond to surface-limited deposition features, similar to UPD, except that they occurred at overpotentials, rather than underpotentials, suggesting slow kinetics [36]. Their corresponding oxidation feature occurred at 0.78 V. The third reduction feature, negative of 0.2 V and down to -0.25 V, corresponds to bulk Se deposition, which oxidized on the positive-going scan in the sharp feature just positive of 0.6 V. The more positive stripping potential (0.78 V) of the Se UPD, the atomic layer of Se in contact with the Au, showed the increased stability, relative to bulk Se (0.6 V), expected for a surface-limited (UPD) process. Negative of -0.25 V, bulk Se was reductively stripped, forming soluble H_2Se in the peak just positive of -0.4 V. The HER on the Se-coated surface began negative of -0.55 V. Compared to the CV for Au in the HMoO_4^- solution (Fig. 2), the HER overpotential on the Se-terminated surface appeared about 0.2 V larger than on the MoO_x -coated surface. Given that Mo electrodeposition appeared hindered by extensive hydrogen evolution, suppressing the HER by coating with Se was felt by the authors to be advantageous for inducing Mo deposition and the formation of MoSe_2 .

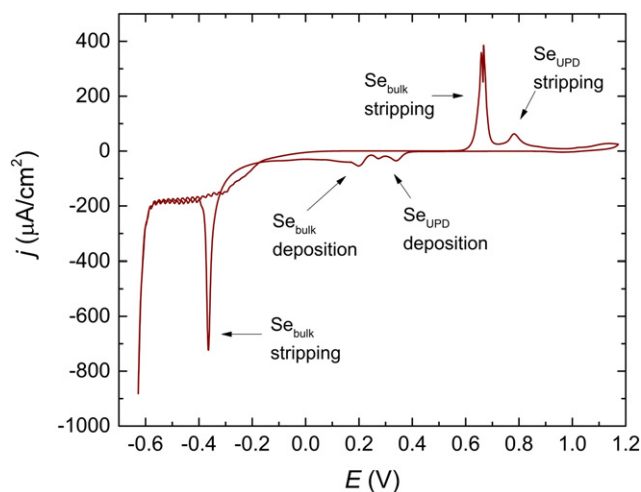


Fig. 5. CV of Au in 0.5 mM SeO_2 and 0.1 M NaClO_4 (pH 1.5). The open-circuit potential was 0.43 V. The potential sweep started in the negative direction from OCP. Se-related reduction and oxidation features are indicated in the CV.

3.2. E-ALD of MoSe_2

In studies of MoSe_2 deposition, the precursor solutions were 0.5 mM SeO_2 and 1 mM HMoO_4^- , both adjusted to pH 1.5. A simplified E-ALD cycle scheme for MoSe_2 formation is shown in Fig. 6. Prior to the first MoSe_2 cycle (the dashed region), Se UPD was formed on the Au substrate by flowing the SeO_2 solution at potential E1 (step a). The cycle was then begun by flowing the HMoO_4^- solution at E1 to deposit MoO_x (step b), followed by the SeO_2 solution, again at E1 (step c). The cycle finished with reduction in the SeO_2 solution at a more negative potential, E2, where the MoO_x was reduced to form MoSe_2 (step d). Any excess (bulk) Se should also have reductively stripped at E2. The E-ALD cycle, steps b to d (Fig. 6), was repeated to grow thicker films. To avoid intermixing the two reactants, a pH 1.5 blank was used between precursor solutions. Current and potential time traces, for one E-ALD cycle, are shown in Fig. 7. The figure also displays solutions and potentials used in each step of the deposition cycle, along with the corresponding current responses.

Oxidative stripping curves were used to characterize preliminary MoSe_2 films, grown using the E-ALD scheme depicted in Fig. 6. The films were formed using $E1 = -0.2$ V and $E2 = -0.4$ V. The voltammetry shown in Fig. 8 was for scans from -0.4 V to 1.5 V. For the purposes of comparison, only films formed with 4-, 5- and 6-cycles are shown. A Gaussian-like oxidation peak was observed in each scan, which shifted positively with increasing number of E-ALD cycles, suggesting increasing stability with the number of cycles, or film thickness. It is important to note that the oxidation peaks occurred at potentials more positive than those for MoO_x or bulk Se oxidation (Figs. 2 and 5). It is presumed that the gain in stability results from the presence of MoSe_2 , a stable compound, as opposed to deposits of the pure elements alone [37,38]. Changes in

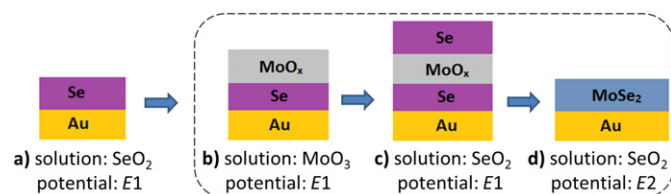


Fig. 6. A simplified scheme for forming MoSe_2 by E-ALD. Se UPD on Au is performed at the beginning of a deposition (step a). Steps b to d are iterated to deposit MoSe_2 in an ALD manner. Blank solution rinse steps were used to avoid intermixing HMoO_4^- and SeO_2 solutions but are excluded in this illustration.

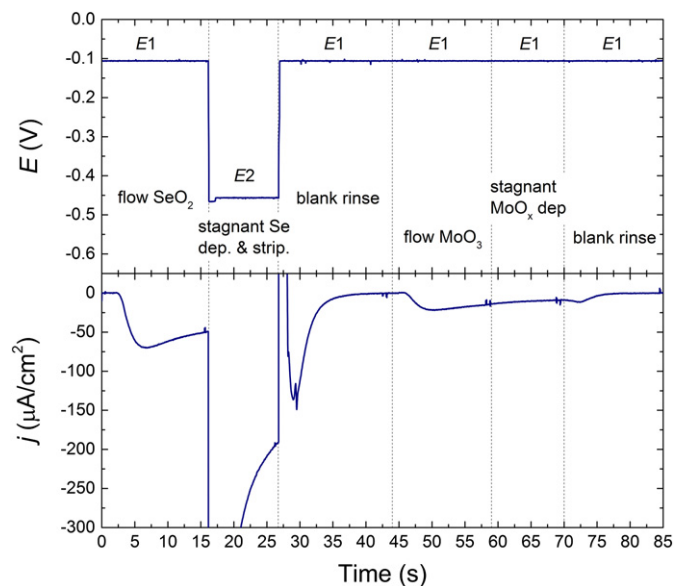


Fig. 7. A representative potential profile (top) used in an E-ALD cycle of MoSe_2 , along with the corresponding current response (bottom) at each step. The vertical dashed lines demarcate the different steps in the cycle. During the solution flow steps, the flow rate was 15 mL min^{-1} . No solution flow occurred during the stagnant deposition steps. $[\text{SeO}_2] = 0.5 \text{ mM}$, $[\text{HMoO}_4^-] = 1 \text{ mM}$. All solutions (pH 1.5) contained 0.1 M NaClO_4 .

the MoSe_2 films' morphology (larger grain sizes, fewer edge sites, etc.) can also lead to the observed stability gain. The relative amounts deposited in each film were quantified by integration of the charge for oxidative stripping, and they are plotted in the inset of Fig. 8, as a function of the number of E-ALD cycles. The linear increase in coverage with cycle number, expected for an ALD process, demonstrates that thicker films can be deposited by increasing the number of cycles.

Photoelectrochemistry (PEC) was used to characterize a 50-cycle film grown using the same cycle conditions used in Fig. 8. In that study the photovoltage was measured as a function of the photoexcitation energy. The photovoltage was essentially a measurement of changes in the electrode's OCP, arising from photogenerated

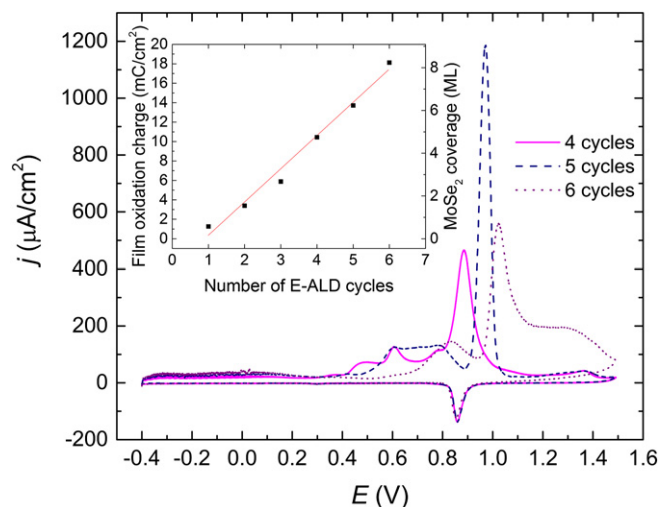


Fig. 8. Oxidative stripping voltammograms in blank solution (0.1 M NaClO_4 ; pH 1.5) of preliminary MoSe_2 films grown by E-ALD. These films were grown by using $E1 = -0.2$ V and $E2 = -0.4$ V. The inset shows the integrated oxidative charge from each film as a function of the number of E-ALD cycles. The MoSe_2 coverage for each cycle was calculated based on a 10-electron oxidation process.

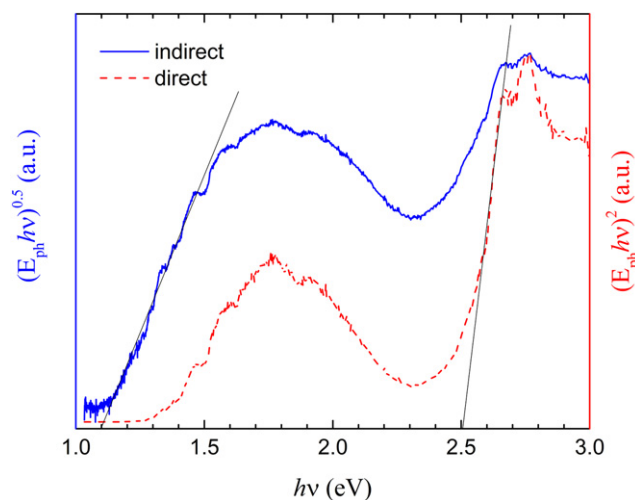


Fig. 9. Photovoltage measurement in 0.1 M NaClO₄ (pH 1.5) of a MoSe₂ film grown by 50 E-ALD cycles. The data was plotted in two different forms that are appropriate for determining either a direct or an indirect band gap. The extrapolated band gap values of 1.1 eV and 2.5 eV correspond to those of MoSe₂ and MoO₃, respectively.

electron-hole pairs [39]. It was used to indirectly probe the absorption of light by the deposit, since the Au substrate was not transparent. The technique proved convenient for characterizing film optical properties. Fig. 9 shows photovoltage, E_{ph} , measurements for the 50-cycle film, where E_{ph} was assumed proportional to the optical absorption coefficient, the premise for plotting data in the form of a Tauc plot for determining an optical bandgap [40]. Two absorption edges suggested the presence of both MoSe₂ and MoO₃ in the film, prompting the construction of two Tauc plots. MoO₃ is known to show a direct transition, while bulk MoSe₂ shows an indirect transition [16,19,41]. Extrapolations of the corresponding absorption edges indicated optical band gaps of 2.5 eV for MoO₃ and 1.1 eV for MoSe₂, which matched literature values well [42].

To optimize deposition potentials in the cycle, E_1 and E_2 , a first series of 50-cycle deposits were prepared by varying E_1 while holding E_2 constant at -0.5 V (Fig. 10). A second series was prepared by varying E_2 while holding E_1 constant at -0.1 V (Fig. 11). Deposit elemental compositions were obtained using EPMA. The Mo content increases as E_1 is pushed negatively, as expected from the CV in Fig. 2. On the other hand, the complementary increase in Se content was not expected from the CV in Fig. 5, as the currents at those values

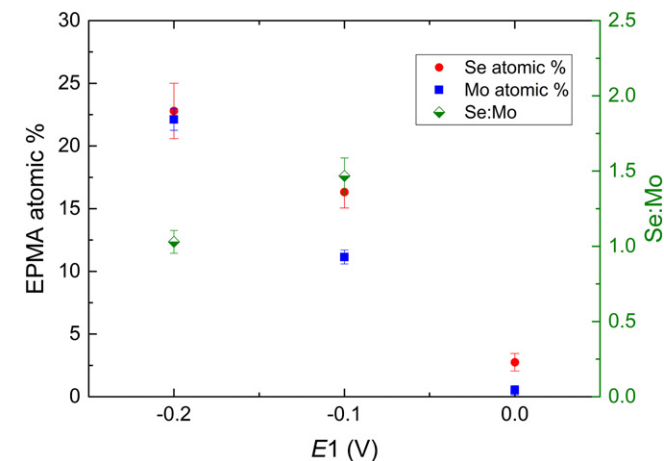


Fig. 10. Composition analysis by EPMA for the series of 50-cycle deposits where E_1 was varied while holding E_2 constant at -0.5 V.

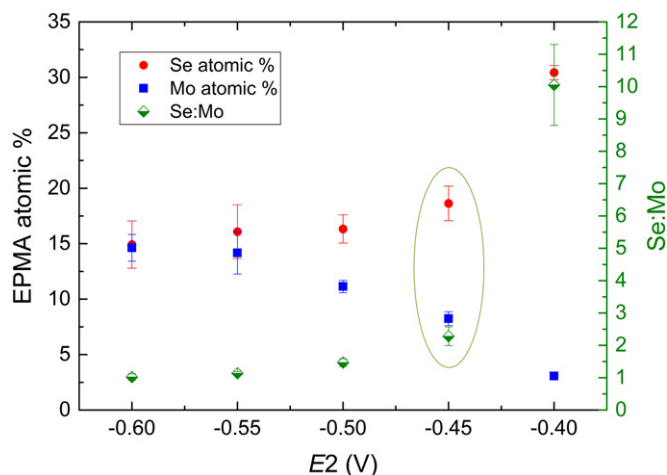


Fig. 11. Composition analysis by EPMA for the series of 50-cycle deposits where E_2 was varied while holding E_1 constant at -0.1 V. The circled composition corresponds to the deposit that had the closest stoichiometric ratio to that of ideal MoSe₂.

of E_1 (from 0 V to -0.2 V) appeared to be the same, i.e., mass-transfer limited. Even if more Se was deposited at the more negative values of E_1 , during the potential step to E_2 (-0.5 V), only Se bound to Mo would be expected to remain on the surface, as any bulk Se (Fig. 5) should have reductively stripped. Those results suggested that as the Mo coverage increased, selenium increased by depositing on the Mo, as would occur in a UPD process.

Fig. 11 shows the composition analysis for the second series of deposits where E_1 was held constant at -0.1 V. E_2 was varied between -0.4 V and -0.6 V. At -0.4 V, the bulk Se was not removed. However, at $E_2 = -0.45$ V, the stoichiometry for Se:Mo is closest to the expected value of 2. At more negative values of E_2 , the coverage of Mo increased and then plateaued, while the Se coverage remained essentially constant. If it is presumed that a MoO_x species is deposited at $E_1 = -0.1$ V, it appears that the kinetics for its reduction with Se to form MoSe₂ are slow and thus potential-dependent. The Mo coverage plateaued at the most negative potentials because the Se coverage was limited during its deposition at E_1 . MoO_x species

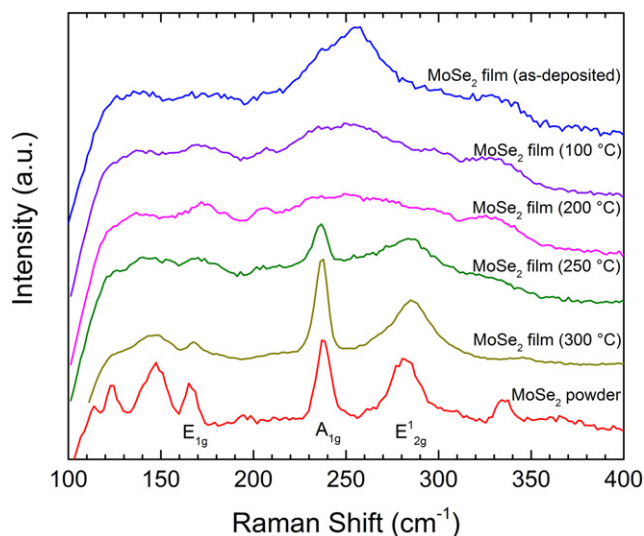


Fig. 12. Micro-Raman spectra of some MoSe₂ films annealed at different temperatures. The characteristic E_{1g} , A_{1g} , and E_{2g}^1 peaks of MoSe₂ are apparent after annealing at 250 °C and above. The spectrum of commercial MoSe₂ powder is included for reference.

not reacted with Se became available for oxidation to a soluble species when the potential was stepped back to -0.1 V (E_1), while any Mo bonded with Se, as MoSe_2 , was stabilized (Fig. 8). From the series shown in Fig. 11, deposits formed using $E_2 = -0.45$ V and $E_1 = -0.1$ V were selected for annealing studies, based on their Se:Mo ratio.

3.3. Annealing studies

Deposits made using $E_1 = -0.1$ V and $E_2 = -0.45$ V were thermally annealed in a 1%/99% H_2/Ar atmosphere. The Raman spectra as a function of annealing temperature are shown in Fig. 12. A broad asymmetric peak centered at 256 cm^{-1} was observed for the as-deposited film. This peak was assigned to a Se-Se stretch mode, arising from a slight Se excess in the film [20]. No other significant changes in the Raman spectra were observed until 250°C or above. At 250°C and above, the well-known E_{1g} , A_{1g} and E_{2g}^1 peaks of MoSe_2 were identified [16,43,44]. Raman spectra from a commercial MoSe_2 powder sample were used for reference.

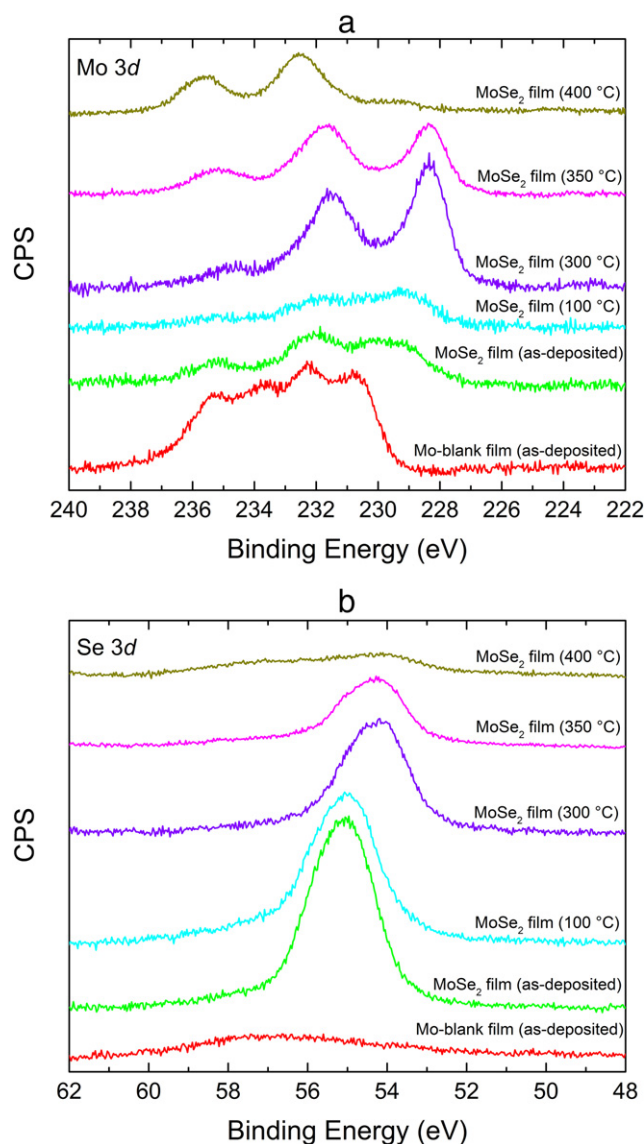


Fig. 13. XPS spectra of the as-deposited and annealed MoSe_2 films showing (a) the Mo 3d and (b) the Se 3d photoelectric peaks. The “Mo-blank” deposit was formed by using the blank instead of the SeO_2 solution within the E-ALD cycles.

XPS was used to follow the effect of annealing on speciation in the surface of the MoSe_2 film. Fig. 13 shows XPS spectra for the Mo 3d and Se 3d regions. The Mo 3d signal from the as-deposited film and the film annealed at 100°C appeared to originate predominantly from Mo oxides on the surface. At 300°C and 350°C , the Mo 3d peaks clearly shifted to lower binding energies, more consistent with Mo in MoSe_2 [20,21,45]. Positions of the Mo $3d_{5/2}$ and Mo $3d_{3/2}$ doublet were 228.4 eV and 231.7 eV , respectively. The Se 3d peaks also exhibited a similar trend as a function of annealing temperature. At 300°C and 350°C , the Se 3d peaks were also shifted to a lower binding energy, consistent with selenide in MoSe_2 . At 400°C , the film was decomposed to form MoO_3 , presumably due to trace oxygen present in the annealing atmosphere [46,47]. Also shown in Fig. 13 are the XPS spectra of a sample made by replacing the SeO_2 solution with blank during deposition. The resulting deposit consisted entirely of MoO_x , which displayed Mo 3d peaks with higher binding energies than those of a normal MoSe_2 deposit, indicating that the Se suppressed Mo oxidation by forming MoSe_2 .

Both Raman and XPS data clearly showed the presence of MoSe_2 in samples annealed at 250°C and above. Although 1% H_2 was used during the annealing in an attempt to provide a reducing environment, its effect was deemed negligible. Samples annealed in pure N_2 also showed similar evidence of MoSe_2 by XPS, even though N_2 would not provide a reducing environment, necessary for the formation of MoSe_2 from MoO_x [19]. Fig. 14 shows the compositions of the annealed deposits from EPMA. As the annealing temperature increased, there was an apparent loss of Se and Mo from the deposits, compared to the as-deposited films. MoSe_2 is thermally stable up to almost 1000°C , so the loss of Se and Mo content was most likely unreacted Se and MoO_x in the deposits [48]. Removal of the Se and MoO_x from the surface by annealing may explain the observed XPS peak shifts. Some MoSe_2 can also be carried off by the gas flux, further contributing to the mass loss. While the annealed samples were amorphous by XRD, their crystallinity could still have been improved by annealing, which would account for the evolution of the MoSe_2 Raman peaks as a function of temperature.

A MoSe_2 sample annealed at 350°C was imaged by STM and SEM. These images are shown in Fig. 15. The disparity in the shapes of the crystallites between the two images suggests that the circular shapes observed in STM were due to a tip effect. Despite the misleading shapes, the height contrast in the STM image does reveal the stacking nature of the flakes in the sample, consistent with the van der Waals character of the 2D material. Fig. 16 shows an SEM image of the STM tip after it was used to image the MoSe_2 sample. Thin MoSe_2

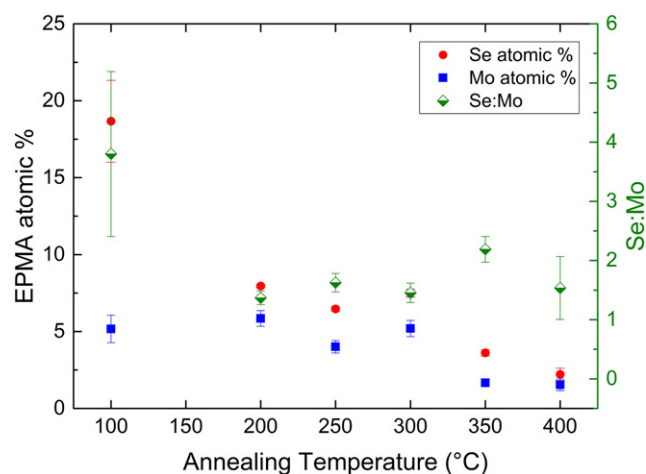


Fig. 14. Composition analysis by EPMA of the films annealed at different temperatures. These films were grown using $E_1 = -0.1$ V and $E_2 = -0.45$ V. Se and Mo losses from the deposits were apparent above 100°C and 300°C , respectively.

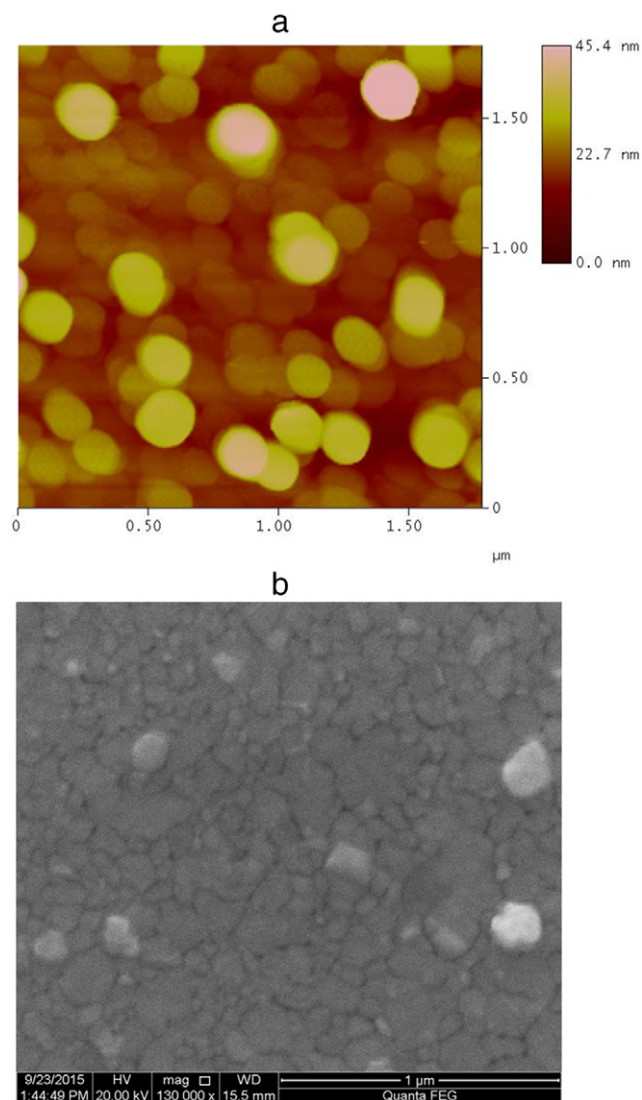


Fig. 15. (a) STM and (b) SEM images of a MoSe₂ sample annealed at 350 °C. The STM image was acquired in air using a tip-sample bias of −300 mV and a tunneling current of 1 nA.

flakes, confirmed by EDS, appear to have become attached to the W tip during STM imaging, presumably owing to their weak adhesion to the substrate. Some of the flakes on the tip resembled the typical rhombic shapes of MoSe₂ and MoS₂ grown by “chemical vapor deposition” (CVD) [19,49–51].

4. Conclusions

The voltammetric behaviors of Au in MoO₃ and SeO₂ solutions were examined under both basic and acidic conditions. Thin films of MoSe₂ were successfully prepared using E-ALD from acidic precursor solutions. PEC photovoltage measurement on the as-deposited films confirmed the presence of MoSe₂ and traces of unreacted MoO₂. Thermal annealing removed the MoO₂, enriching the films in MoSe₂, as confirmed using XPS. The evolution of MoSe₂ Raman peaks as a function of temperature showed that the crystallinity of the films were improved by annealing, though they still appeared amorphous by XRD. Although the film growth conditions have not been fully optimized, this report demonstrated that E-ALD can be used to grow MoSe₂ films. Use of Se to induce the deposition of Mo in order to

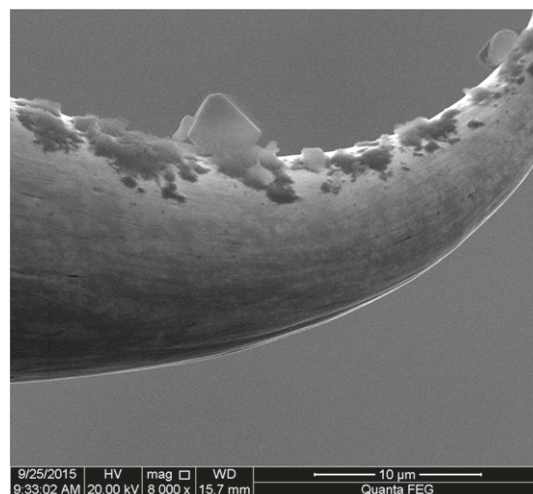


Fig. 16. SEM of the STM tip after it was used to image the MoSe₂ sample in air. MoSe₂ flakes, confirmed by EDS, were adhered onto the interior of the tip's curvature.

electrochemically grow MoSe₂ might be applicable to the growth of other transition metal dichalcogenides (TMDC).

Acknowledgments

Support for this work, from NSF ECCS, award number 1124733, is gratefully acknowledged. Helpful discussions from Chris Fleisher and for the use of the UGA Electron Microprobe Lab are appreciated. Dr. Zhengwei Pan is also appreciated for the use of his SEM.

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