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## Non-vacuum Preparation of $\text{WSe}_2$ Thin Films *via* the Selenization of Hydrated Tungsten Oxide Prepared using Chemical Solution Methods

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### ABSTRACT

*It is known that tungsten oxide may be reacted with selenium sources to form  $\text{WSe}_2$  but literature reports include processing steps that involve high temperatures, reducing atmospheres, and/or oxidative pre-treatments of tungsten oxide. In this work, we report a non-vacuum process for the fabrication of compositionally high quality  $\text{WSe}_2$  thin films via the selenization of tungsten oxide under milder conditions. Tungsten source materials were various hydrated  $\text{WO}_3$  and  $\text{WO}_{2.9}$  compounds that were prepared using chemical solution techniques. Resulting films were selenized using a two-stage heating profile (250 °C for 15 minutes and 550 °C for 30 minutes) under a static argon atmosphere. Effects of the starting tungsten oxide phase on  $\text{WSe}_2$  formation after single and double selenization cycles were investigated using Raman spectroscopy and X-ray diffraction (XRD). After two selenization cycles, hydrated  $\text{WO}_3$  was converted to (002)-oriented  $\text{WSe}_2$  that exhibits well-resolved peaks for  $E_{2g}^1$  and  $A_{1g}$  phonon modes. Only a single selenization cycle was required to convert amorphous  $\text{WO}_{2.9}$  to  $\text{WSe}_2$ . All selenizations in this work were achieved in non-reducing atmospheres and at lower temperatures and shorter times than any non-laser-assisted processes reported for  $\text{WO}_3$ -to- $\text{WSe}_2$  conversions.*

### INTRODUCTION

With its low mineral extraction costs [1], a reported direct bandgap of 1.35-1.5 eV [2] and high minority carrier mobility [3], the  $\text{WSe}_2$  material system is seeing renewed interest in next-generation solar cell absorber material development. Heterojunction photovoltaic (PV) devices based on  $\text{WSe}_2$  single-crystal absorbers have had reported efficiencies exceeding 8% [4]. Fabrication of  $\text{WSe}_2$  films *via* the selenization of tungsten has been shown to be effective at temperatures > 900 °C and reaction times longer than 24 hrs [5] due to a large activation energy barrier that accompanies the lattice expansion. So-called “soft selenization” of tungsten [3,6] at temperatures of 450-560 °C over 24 hrs has yielded  $\text{WSe}_2$  films of non-specific orientation and there is no evidence for electronic properties that would be suitable for

PV applications. More recently, a laser-assisted selenization method has been successfully executed at 250 °C, but this is useful only in conjunction with small-spot targeting [7].

It is known that tungsten oxide may be reacted with various selenium sources to form WSe<sub>2</sub> but literature reports still include processing steps that involve high temperatures and/or reducing atmospheres [8-14]. Selenization temperatures of evaporated WO<sub>3</sub> films have been reduced from 950 to 800 °C after the inclusion of a Ni backlayer that forms one or more relatively low-temperature melting NiSe<sub>2-x</sub> phases which act as intermediates in WSe<sub>2</sub> formation [15]. Selenization of native WO<sub>3</sub> films on tungsten have been reported at 650 °C in a reducing atmosphere [16]. It has been proposed that the initial step in this mechanism is the reaction between H<sub>2</sub> and WO<sub>3</sub> to produce oxygen-deficient WO<sub>3-x</sub> species that undergo thermodynamically favorable substitutions of oxygen by selenium.

We have discovered that the nature of the WO<sub>3</sub> precursor film can significantly affect the minimum time and temperature requirements for selenization. In this report, we describe the results of selenization of various WO<sub>3</sub> and WO<sub>2.9</sub> compounds prepared using chemical solution methods. Heating these films in the presence of excess Se in a non-reducing argon atmosphere at temperatures no higher than 550 °C for heating/dwelling/cooling times totaling no more than 3 hours results in partial or complete conversion to WSe<sub>2</sub>. No dynamic vacuum, inert gas flow, or higher-temperature post-anneal is required. Raman spectra and XRD patterns consistent with those for films prepared by higher-temperature and longer-time selenization of evaporated WO<sub>3</sub> films.

## EXPERIMENT

### Hydrated WO<sub>3</sub> (HTO) preparation [17]

A solution of 3 mL diethyl sulfate (Aldrich, 98%), 87 mL deionized water and 1.65, 2.15 or 2.50 g of Na<sub>2</sub>WO<sub>4</sub> · 2H<sub>2</sub>O (Mallinckrot) was prepared, heated to 90 °C with stirring and held at that temperature for five minutes. The resulting yellow or yellow-white particle suspension was transferred to a 50-mL centrifuge tube containing a 1-inch diameter Corning 1737F glass disk at the bottom. Particle deposition was achieved through centrifugation [18] at 2000g for eight minutes. The resulting yellow-white films were visibly particulate and scratched easily, so thickness measurements were not possible.

### WO<sub>2.9</sub> (blue tungsten oxide or BTO) preparation [19].

A dip-coating solution was prepared by combining 2 g WCl<sub>6</sub> (Aldrich, 99.9%) and 20 mL anhydrous ethanol (Pharmco-Aaper) and the resulting blue solution was stirred for several hours prior to dip coating (12.5 mm/s speed) onto 1-inch Corning 1737F glass disks. The resulting blue films were visibly smooth and translucent but scratched easily, so thickness measurements were not possible.

### Selenization and film characterization.

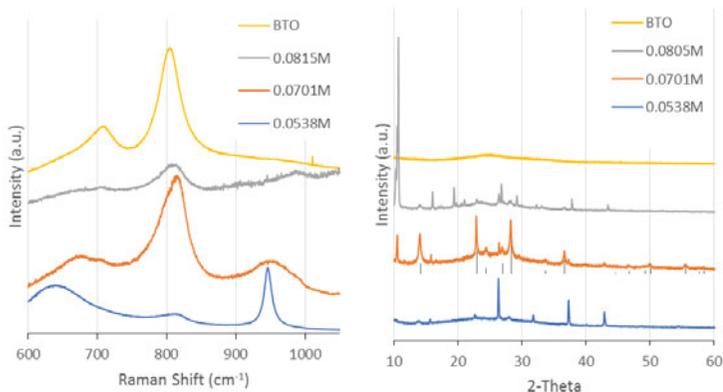
Coated substrates were placed in a graphite susceptor containing excess Se and heated under an argon atmosphere. The sample temperature was increased by 25 °C/min to 250 °C and held there for 15 minutes. This was followed by another 25 °C/min ramp to 550 °C where, unless otherwise specified, the sample dwelled for 30 minutes then cooled to room temperature over 1 hour. This entire process will be referred to as a

selenization “cycle”. After characterization by Raman spectroscopy and x-ray diffraction (XRD), the film was subjected to a second identical selenization cycle unless otherwise specified. Some degree of flaking and thickness inhomogeneities were observed in the gray product films, which scratched easily upon attempts to remove samples for electron microscopy analysis.

## RESULTS AND DISCUSSION

Three samples of HTO materials were prepared by varying the initial solution  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  concentrations (0.0538, 0.0701, 0.0815 M). No steps were taken to buffer pH levels which were initially 8.34, 8.63, and 8.79, respectively, and decreased by approximately 2 units during the heating and HTO formation processes due to  $\text{H}_3\text{O}^+$  release by diethyl sulfate [20]. Raman spectra (Figure 1, left) of these samples show peaks in the 600–850  $\text{cm}^{-1}$  region due to O–W–O bending modes and a peak at 950  $\text{cm}^{-1}$  from surface W=O bond stretching [21]. This last peak is most intense in the 0.0538 M sample and the general spectral shape is consistent with the dihydrate form of  $\text{WO}_3$ . As the sodium tungstate concentration was increased, this peak diminished in intensity and the lower O–W–O bending frequency shift higher to match what has been reported for the monohydrate  $\text{WO}_3$  form [21]. The XRD pattern (Figure 1, right) of the 0.0701 M sample indicates that it consists mainly of hexagonal  $\text{WO}_3 \cdot 1/3\text{H}_2\text{O}$  [22] while the other HTO sample patterns do not match well with any in single-phase JCPDS cards. The 0.0701 and 0.0815 M samples exhibit intense peaks at  $2\theta = 10.49^\circ$  and  $10.65^\circ$ , respectively. These are consistent with reported reflections from oxygen-deficient species such as  $m\text{-W}_{18}\text{O}_{49}$  (200) [23] and  $\text{H}_{12}\text{W}_{12}\text{O}_{42} \cdot 21\text{H}_2\text{O}$  (111) [24]. The formation of the latter compound would be consistent with a previously proposed mechanism for this reaction [20]. Using Scherrer’s formula [25], crystallite sizes were estimated to be 45–60, 25–50, and 65–90 nm for the 0.0538, 0.0701, 0.0815 M samples, respectively.

The reaction of  $\text{WCl}_6$  and anhydrous ethanol results in the formation of a deep blue solution consisting of  $\text{WO}_{2.9}$  (BTO) [19]. This oxygen deficiency results in the partial reduction of tungsten and creates a low-energy  $\text{W}^{5+}$ -to- $\text{W}^{6+}$  intervalence charge transfer transition leading to the blue color [26]. After dip-coating, the resulting sample



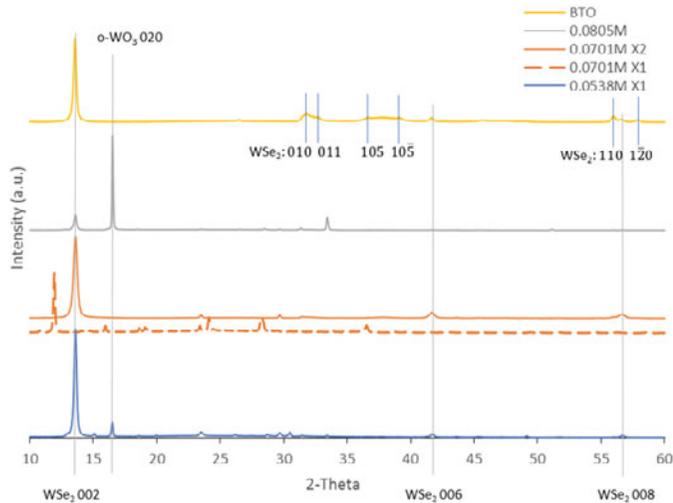
**Figure 1.** Raman spectra (left) and XRD patterns (right) of as-made BTO films and HTO films prepared from 0.0815, 0.0701, and 0.0538 M  $\text{Na}_2\text{WO}_4$  solutions, respectively. Legend orders match the spectrum/pattern orders top-to-bottom. The vertical lines under the 0.0701 M XRD pattern are from JCPDS card no. 35-1001 for hexagonal  $\text{WO}_3 \cdot 1/3\text{H}_2\text{O}$ .

exhibited no significant XRD peaks and only O-W-O bending modes ( $710, 806 \text{ cm}^{-1}$ ) were present in the Raman spectrum (Figure 1, left).

Each sample was selenized under identical conditions as described in the Experiment section. After one selenization cycle, the  $0.0538 \text{ M}$  sample was partially converted to  $\text{WSe}_2$ . The XRD pattern (Figure 2) exhibits prominent peaks assigned to the 002, 006, and 008  $\text{WSe}_2$  reflections; however, noticeable peaks at  $2\theta = 16.5^\circ$  and  $24\text{--}30^\circ$  due to orthorhombic and monoclinic  $\text{WO}_3$ , respectively, are also present. The Raman spectrum (Figure 3), reveals the presence of  $\text{WSe}_2$  with distinguishable  $E_{2g}^1$  and  $A_{1g}$  mode peaks at  $250$  and  $255 \text{ cm}^{-1}$ . Spectral separation of these modes has been linked to mobility carrier properties that are promising for photovoltaic applications [27].

After a second selenization cycle, the  $\text{WO}_3$  (Raman, XRD) and Se (Raman) peaks were no longer present and the  $\text{WSe}_2$   $E_{2g}^1$  and  $A_{1g}$  mode peaks were shifted to  $248$  and  $252 \text{ cm}^{-1}$ , respectively. These are consistent with frequencies reported for  $\text{WSe}_2$  thin films and the shift indicates the relief of lattice strain during the second selenization cycle [10]. Peaks stemming from  $A_{1g}$ -LA modes [28] at  $371$  and  $393 \text{ cm}^{-1}$  are much more prominent.

Selenization (one cycle) of the  $0.0701 \text{ M}$  sample results in a Raman spectrum (Figure 3) that shows only  $\text{WSe}_2$  peaks with the possible exception of a small peak at  $910 \text{ cm}^{-1}$  that could be due to  $\text{W}=\text{O}$  stretching from residual  $\text{WO}_3$  that is also apparent from XRD peaks (Figure 2) at  $2\theta = 24.16^\circ$  and  $28.33^\circ$  ( $m\text{-WO}_3$ ). The most prominent XRD

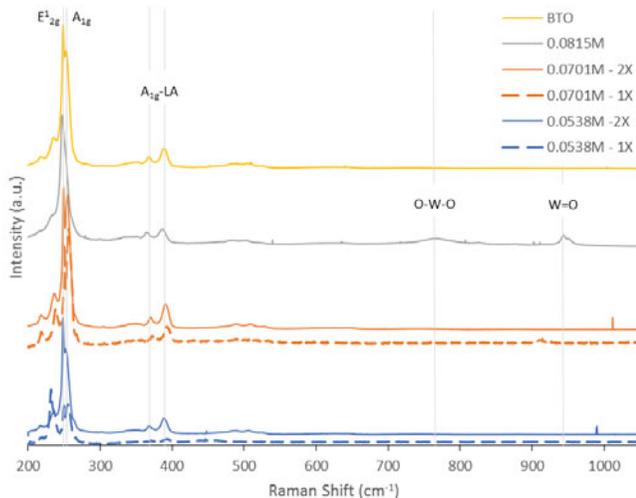


**Figure 2.** XRD patterns of selenized BTO films and HTO films prepared from  $0.0815$ ,  $0.0701$ , and  $0.0538 \text{ M}$   $\text{Na}_2\text{WO}_4$  solutions, respectively. Legend orders match the spectrum order top-to-bottom. 1X = one selenization cycle, 2X = two selenization cycles.

peak is at  $2\theta = 11.94^\circ$ . While this angle does not match those for any reported  $\text{WSe}_2$  reflections [29], it is possible that unit cell compression shifted the 002 peak from its typical  $2\theta = 13.7^\circ$  angle. After a second selenization cycle, a well-oriented  $\text{WSe}_2$  results as indicated by prominent 002 ( $2\theta = 13.77^\circ$ ), 006 ( $41.56^\circ$ ), and 008 ( $56.44^\circ$ ) reflections at expected angles. The Raman spectrum shows slight red shifts of the  $E_{2g}^1$  and  $A_{1g}$  phonon

mode frequencies by 1-2  $\text{cm}^{-1}$ . Interestingly, doubling the 550 °C dwell time during the first selenization does not remove the residual  $\text{WO}_3$  from the sample that was observed after one of our standard selenization cycles. It is possible that the cooldown step between the first and second selenization cycles induces the crystallization of a strained  $\text{WSe}_2$  lattice, perhaps due to incomplete oxygen displacement or the presence of residual  $\text{WO}_3$ , that is more reactive to further selenization. Further investigation is in process.

After one selenization cycle, the 0.0815 M sample exhibited Raman peaks (Figure 3) due to  $\text{WSe}_2$  ( $E_{2g}^1/A_{1g}$  modes at  $247 \text{ cm}^{-1}$ ) and  $\text{WO}_3$  (O-W-O bending at  $765 \text{ cm}^{-1}$  and W=O stretching at  $944 \text{ cm}^{-1}$ ). The XRD pattern (Figure 2) shows prominent peaks from  $\text{WSe}_2$  002 ( $2\theta = 13.61^\circ$ ) and 011 ( $33.43^\circ$ ) as well as the (020) reflection ( $16.54^\circ$ ) from o- $\text{WO}_3$ . A second selenization does not affect these spectra.



**Figure 3.** Raman spectra of selenized BTO films and HTO films prepared from 0.0815, 0.0701, and 0.0538 M  $\text{Na}_2\text{WO}_4$  solutions, respectively. Legend orders match the spectrum order top-to-bottom. 1X = one selenization cycle, 2X = two selenization cycles.

A single selenization of the BTO film results in XRD and Raman peaks that can all be assigned to  $\text{WSe}_2$ . In the XRD pattern (Figure 2), the (002) reflection is the most prominent but the presence of several non-c-axis-oriented reflection plane peaks indicates that the film is not as well-oriented as the double-selenized 0.0538 and 0.0701 M HTO samples. The Raman spectrum (Figure 3) does feature distinguishable  $E_{2g}^1$  and  $A_{1g}$  mode peaks at  $248$  and  $252 \text{ cm}^{-1}$ .

All selenizations in this work were achieved in non-reducing atmospheres and at lower temperatures and shorter times than any non-laser-assisted processes reported for  $\text{WO}_3$ -to- $\text{WSe}_2$  conversions. Thermodynamically, selenization of  $\text{WO}_x$  in non-reducing atmospheres becomes favorable when  $x < 2$  [16]. While there is no evidence of such species present during these reactions, our observations may lend insight about kinetic factors that could lower activation energies. Access of selenium vapor to tungsten atoms in the crystal lattice may be important. This may be facilitated by the particulate and somewhat porous nature of our films. However, hydration of  $\text{WO}_3$  structures opens spaces between planes of tungsten coordination units in the crystal

lattice [21]. There is also the possibility of Se reacting with these waters of hydration to form trace quantities of H<sub>2</sub>Se that may act as an intermediate in the selenization mechanism [10]. In the case of WO<sub>2.9</sub> selenization, a greater number of oxygen-deficient WO<sub>x</sub> sites may lead to faster reactivity, possibly through defect-induced partial encapsulation mechanisms [30].

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