Analysis of Raman and Ellipsometric Responses of \( \text{Nb}_x \text{W}_{1-x} \text{Se}_2 \) alloys

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Abstract: The growth of transition metal dichalcogenide (TMDC) alloys provides an opportunity to experimentally access information elucidating how optical properties change with gradual substitutions in the lattice compared with their pure compositions. In this work, we performed growths of alloyed crystals with stoichiometric compositions between pure forms of \( \text{NbSe}_2 \) and \( \text{WSe}_2 \), followed by an optical analysis of those alloys by utilizing Raman spectroscopy and spectroscopic ellipsometry.

Keywords: ellipsometry; Raman spectroscopy; transition metal dichalcogenides

1. Introduction

The category of materials known as transition metal dichalcogenides (TMDCs) has been the subject of intense study in recent years, with latest efforts focusing on the quantum confinement in two dimensions resulting in direct bandgaps [1-7] and well-defined many-body effects [8-10]. Because TMDCs have wide-ranging applicability in photovoltaics, spintronics, optoelectronics, and energy storage [11-14], the ability to control and manipulate various facets of their inherent properties is strongly desired. Furthermore, this family of materials can be catalogued into several groups based on their characteristic electrical behavior. Semiconducting TMDCs, such as \( \text{WSe}_2 \), exhibit phenomena including coupled spin and valley degrees of freedom [15-18], whereas metallic TMDCs, such as \( \text{NbSe}_2 \), display properties such as charge density waves and superconductivity [19-27]. When alloyed, these materials offer advantages ranging from the control of a semiconductor’s carrier density, construction of flexible gas sensors, and fabrication of 1D edge contacts or junctions [32-36]. Though the pure forms of \( \text{NbSe}_2 \) and \( \text{WSe}_2 \) have been well-studied optically [37-43], their alloys need more assessments [32-33, 44-47].

In this work, three optical spectroscopies were used to evaluate alloyed \( \text{Nb}_x \text{W}_{1-x} \text{Se}_2 \) crystals grown using chemical vapor transport (CVT). Samples exfoliated from these crystals were characterized with energy-dispersive X-ray spectroscopy (EDS) and Raman spectroscopy. An analysis of the optical, in-plane dielectric function \( \varepsilon(E) \) was conducted using data acquired with spectroscopic ellipsometry (SE).
2. Experimental Methods

2.1 Crystal Growth and Energy-Dispersive X-ray Spectroscopy

Nb$_x$W$_{1-x}$Se$_2$ single-crystals on the centimeter scale were grown using CVT. Appropriate amounts of Nb (99.9 %), W (99.9 %) and Se (99.999 %) powders with a total weight of about 1 g were vacuum-sealed in a quartz ampoule with approximately 100 mg of SeBr$_4$ (99 %) as a transport agent. All precursors were purchased from Strem Chemicals, Inc.¹ Next, the ampoules were placed in a single-zone furnace so that the temperature at the charge zone and the growth zone was 980 °C and 850 °C, respectively. The ampoules were cooled down by switching off the furnace after 6 d of growth. All grown crystals were mechanically exfoliated onto fused silica substrates. Due to the limitations on both the equipment and the solid solubility, concentrations of Nb in the mid-range were unable to successfully be grown.

EDS analyses were performed on the bulk crystals directly after growth using a JEOL JSM-7100F field-emission scanning electron microscope equipped with an Oxford Instruments X-Max 80 silicon drift detector and a FEI Quanta 200 scanning electron microscope equipped with a Bruker XFlash 5030 silicon drift detector at a 10 keV accelerating voltage.

2.2 Raman Spectroscopy

Raman spectroscopy was performed on freshly exfoliated crystals (taken from bulk crystals) of each composition (approximately 100 nm thick). Raman spectra were collected with a Renishaw InVia micro-Raman spectrometer using a 514.5-nm wavelength excitation laser source. The laser was fixed at a constant power of 500 μW and had a spot size of about 1 μm. Acquisition times varied between 10 min and 30 min, and the optical path included a 50 × objective and 1200 mm$^{-1}$ grating. Rectangular Raman maps were collected at room temperature in a backscattering configuration with step sizes of 5 μm in a 5 by 3 raster-style grid.

2.3 Spectroscopic Ellipsometry

SE measurements were performed on freshly exfoliated crystals (taken from bulk crystals) all compositions with a Woollam M-2000 Ellipsometer, Model XI-210, and its 75 W Xenon light source comprising wavelengths between about 210 nm to 1000 nm (1.24 eV to 5.88 eV) with 1.25 nm resolution. The elliptical spot size measured approximately 100 μm along the semi-minor axis and 200 μm to 300 μm along the semi-major axis. SE measures the change in phase and polarization state of light reflected from a

¹ Commercial equipment, instruments, and materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology or the United States government, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.
sample of interest. Each crystal was measured over 20 times to directly extract $\varepsilon(E)$. Data were acquired at two angles of incidence (60° and 70°) and subsequently converted by the software from Fresnel reflection coefficients, representative of $p$ and $s$ polarized light ($R_p$ and $R_s$), to the related quantities psi and delta ($\Psi$ and $\Delta$), where $\frac{R_p}{R_s} = e^{i\Delta} \tan \Psi$. The dielectric function of each alloyed crystal was then converted from psi and delta directly.

3. Characterization of Alloyed Crystals

EDS data are shown in Fig. 1 on a logarithmic vertical scale and are taken for each of the $\text{Nb}_x\text{W}_{1-x}\text{Se}_2$ crystals of mixed composition, with the main relevant responses occurring between 1 keV and 2.5 keV. The response from Se (green band) remains unchanged as expected, whereas the W (purple band) decreases in relative intensity as the material approaches pure NbSe$_2$. In the case of Nb (orange band) the signal strength does decrease with Nb atom concentration, but for the top two panels, he presented concentrations of $x^{(1)}$ and $x^{(2)}$ are Nb peaks that were too difficult to distinguish since the detection limit of the measurement was exceeded. Though the Nb peaks still appear albeit just barely above the detection limit, determining an accurate concentration of Nb is not feasible from these data.
Fig. 1. EDS spectra are shown for the various CVT-grown crystals of mixed composition with the concentration labeled on the right (values of $x$ include $x^{(1)}$, $x^{(2)}$, 0.74, 0.85, and 0.92). The primary Se, W, and Nb responses are marked within the green, purple, and orange shaded regions, respectively. One can extract the compositions for the bottom three panels with better accuracy than the top two panels, whose compositions are not directly measurable.

As established, Raman spectroscopy is a noninvasive technique that can probe a variety of 2D materials on various substrates over large distances [48-50]. Figure 2 (a) shows the Raman spectra of the various modes which arise for the CVT-grown crystals with their corresponding Nb concentrations ($x$) labeled on the right. In all spectra, Raman modes were fit with Lorentzian peaks to extract the Raman shift and the full width at half maximum (FWHM). The pink shaded region highlights the most dynamic changes in the spectra. Each pure TMDC exhibits its $A_{1g}$ and $E_{2g}$ modes within this region, with WSe$_2$ also exhibiting the 2LA(M) mode at approximately 262 cm$^{-1}$. In the case of the WSe$_2$ $A_{1g}$ and $E_{2g}$ modes, located at approximately 258 cm$^{-1}$ and 249 cm$^{-1}$, respectively, they persist until Nb concentration values above $x = 0.74$ is achieved, with the latter mode persisting until W concentrations fall beneath 8% ($x = 0.92$). A similar observation is made with the $A_{1g}$ and $E_{2g}$ modes of NbSe$_2$, with the former (at about 232 cm$^{-1}$) being the first to vanish as $x$ decreases and the latter (at about 241 cm$^{-1}$) persisting for low values of $x$ and finally vanishing in the case of pure WSe$_2$. These trends in Raman shift are shown in Fig. 2 (b). For Fig. 2 (c), the same five modes have their FWHM displayed as a function of $x$. Though many of the peak
widths remain relatively stable in the interval $0 < x < 0.92$, some of the peaks demonstrate an abrupt increase in width as $x$ approaches 1.

Modes for WSe$_2$ at approximately 360 cm$^{-1}$, 375 cm$^{-1}$, and 395 cm$^{-1}$ are of second-order, and their respective assignments follow. The first mode is either a 2E$_{1g}(\Gamma)$ or an A$_{1g}(M)$+TA(M) [48], with an alternate assignment of 2E$(\Gamma)$–LA(K) and 2A$_1$(\Gamma)–LA(K) [40]. The second mode has been reported as an E$_{2g}(M)$+LA(M), E$(\Gamma)$+LA(M), and A$_1$(\Gamma)+LA(M), and the third mode consists of an E$(\Gamma)$+LA(K), A$_1$(\Gamma)+LA(K), and 3LA(M) [40, 51]. These first two modes more rapidly vanish with increasing Nb concentration, but the third mode appears to persist up to about $x = 0.74$. Comparison of these modes with those in the literature is crucial to help verify that the alloys are taking on the approximate stoichiometric values for which they have been grown.

![Fig. 2](image.png)

**Fig. 2.** (a) Raman spectra are shown for the various CVT-grown crystals with the concentration labeled on the right (values of $x$ include 0, $x^{(1)}$, $x^{(2)}$, 0.74, 0.85, 0.92, and 1). (b) The five modes of interest in the pink shaded region of (a) were fit with Lorentzian peaks to extract the shift and FWHM. A$_{1g}$ and E$_{2g}$ modes for both NbSe$_2$ and WSe$_2$ (and the 2LA(M) for the latter) are plotted as a function of Nb concentration $x$. (c) The FWHM of each mode is plotted as a function of $x$. The symbols (and their outer colors) are
identical to their corresponding representations in (b). Error bars for the FWHM data represent the 1σ uncertainty of the width of the peak based on the Lorentzian fits.

4. Dielectric Properties

4.1 SE Measurements

By performing SE measurements, additional optical properties such as the dielectric function ($\varepsilon(E) = \varepsilon_1(E) + i\varepsilon_2(E)$), refractive index ($n$), and extinction coefficient ($\kappa$) can be obtained. Figure 3 shows the data acquired with 100-nm-thick, bulk samples on fused quartz. In cases where the material of interest is on a transparent substrate, the process for determining quantities like absorption, reflection, or transmission is substantially easier, further extended the ease with which one can observe excitons and other optical phenomena [51-54]. Excitons are generally seen easily through absorption spectra, which are themselves primarily determined by the imaginary component of the dielectric function ($\varepsilon_2$) and related by $\frac{\varepsilon_2}{A(E)} = \frac{hc}{EL}$, where $E$ is the energy and $L$ is the layer thickness [53].
Fig. 3. SE measurements of $\Psi$ and $\Delta$ are converted such that the imaginary part of the dielectric function $\varepsilon_2(E)$ is shown for each of seven compositions of $\text{Nb}_x\text{W}_{1-x}\text{Se}_2$ alloy as a function of energy. As the Nb concentration $x$ is increased from 0 to 1, $\varepsilon_2$ transitions from semiconducting $\text{WSe}_2$ to metallic $\text{NbSe}_2$. The phenomena to note are the changes in the $A$ and $B$ exciton, labelled $X_0^A$ (azure region) and $X_0^B$ (orange region), respectively. The $C$ and $D$ transitions are also labelled as $X_0^C$ (red region) and $X_0^D$ (lavender region), respectively. The shaded green regions around each curve represent a $1\sigma$ uncertainty.

Measurements were performed on samples that were freshly cleaved to prevent oxidation effects (see Appendix A). Among the advantages of performing SE on an exfoliated bulk crystal to obtain optical information, two of them are most relevant. First, the thickness does not need to be known to within nanometers because the calculated optical constants ($n$ and $\kappa$) do not change with perturbations to bulk thickness. Furthermore, the incoming light interacts with a single crystal material as opposed to a layered dielectric. In the latter case, $\Psi$ and $\Delta$ would generate a pseudo-dielectric function representing a hybrid material and thus not an accurate representation of the measured sample. In our case, the requirement of precise layer-by-layer analysis is greatly alleviated and $\Psi$ and $\Delta$ generate the actual dielectric function of each measured alloy.
Figure 3 shows the results of converting SE measurements of $\Psi$ and $\Delta$ to $\varepsilon_2(E)$. The $A$ and $B$ exciton of WSe$_2$, which are representative of spin-split bands at the K/K' point, are labelled $X^0_A$ (azure region) and $X^0_B$ (orange region) in Fig. 3, respectively. Additionally, the $C$ and $D$ transitions of WSe$_2$ are respectively labelled $X^0_C$ (red region) and $X^0_D$ (lavender region) in Fig. 3. The bottom four panels show that as NbSe$_2$ becomes W-rich, diverging from its pure form, $\varepsilon_2$ also gradually increases over the whole spectrum until $x = 0.74$ when the changes in the alloy’s local band structure become more substantial to accommodate for the increased concentration of W atoms.

4.2 Optical Constants and Comments on the Low Nb Concentration

The Nb concentrations for the two lowest values fell below the EDS limit of detection, but due to observed spectral changes, and most prominently from the broadening of $X^0_A$, introduction of Nb atoms to what would have otherwise been a pure WSe$_2$ crystal is a more likely scenario. We compared our result to the same system in another work in which broadening of $X^0_A$ by approximately 50 meV for Nb-doped WSe$_2$ was observed [33]. Our observed broadening of $X^0_A$ was about 38 meV and 63 meV for $x^{(1)}$ and $x^{(2)}$, respectively, as seen in the two central panels of Fig. 4 (a). It is crucial to stress that though the exact concentration cannot be directly measured as prepared, the fact that $x^{(1)} > x^{(2)}$ suggests that $x^{(1)}$ may represent a slightly smaller concentration since the alloy more closely resembles its pure counterpart (WSe$_2$).

To expand on the optical properties of these alloys, more practical representations of how light propagates through these were calculated. In Fig. 4 (b), the full dielectric function was transformed into optical constants and were calculated for each of the seven compositions, with $n$ shown in blue (left vertical axis) and $\kappa$ in pink (right vertical axis). These constants can be easily applied to determine additional quantities such as the absorption, reflection, or transmission spectra.
Fig. 4. (a) A spectral region covering energies between 1.25 eV and 3.25 eV is shown for four of seven compositions. Lorentzian fits are applied to each curve to extract the position and width of the $A$ and $B$ excitons, labeled $X^0_A$ (light blue curve) and $X^0_B$ (light green curve), respectively. The $C$ and $D$ transitions are not shown for clarity but have been included in the fitting procedure. (b) Optical constants are calculated for each of the seven compositions, with the refractive index $n$ shown in blue (left vertical axis) and the extinction coefficient $\kappa$ in pink (right vertical axis).

5. Conclusions

In summary, we performed several growths of alloyed crystals with stoichiometric compositions between pure forms of NbSe$_2$ and WSe$_2$. An optical analysis of those alloys was performed by utilizing energy-dispersive X-ray spectroscopy, Raman spectroscopy, and spectroscopic ellipsometry. The imaginary dielectric function was extracted from the ellipsometric data, revealing the extent of spectral changes present in the alloys as a function of transition metal concentration.

6. Appendix A

More details regarding the oxidation effects present in exfoliated flakes from the CVT NbSe$_2$ crystal are provided here. Photoluminescence (PL) spectra are visible for the material after one day of exposure to air, highlighting the importance of encapsulation, fast measurement, or immediate placement of freshly exfoliated flakes into an oxygen-free environment. Figure 5 summarizes the PL results as a function of power for both CVT and commercially-obtained flakes. The PL peak arises from the presence of NbO$_2$ and the rate of oxidation appears to scale non-linearly with power [55]. All measurements use flakes that were significantly less exposed to air than the full day after which oxidation PL becomes noticeable.
Fig. 5. (a) The power-dependent PL spectra are shown here to verify that the large feature around 1.75 eV is likely representative of NbO$_2$ formation resulting from the exposure of the CVT-grown crystal to air for one day. This highlights the importance of performing all optical measurements immediately after exfoliation. (b) When comparing the PL spectrum of the CVT-grown (purple) and commercially-obtained crystal (cyan), both experience the same level of oxidation after one day in air. This supports the idea that the air sensitivity of the crystals is likely inherent to the material.

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7. References

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