A Method Toward Fabricating Semiconducting 3R-NbS₂ Ultrathin Films

Jatis K. Dash,^{*,†} Liang Chen,[†] Peter H. Dinolfo,[‡] Toh-Ming Lu,[†] and Gwo-Ching Wang[†][†]Department of Physics, Applied Physics and Astronomy, and [‡]Department of Chemistry and Chemical Biology, Rensselaer Polytechnic Institute, 110 8th Street, Troy, New York 12180, United States

Supporting Information

ABSTRACT: Ultrathin NbS₂ films were synthesized from sputter-deposited ultrathin Nb films on SiO₂/Si and quartz substrates at 850 °C under sulfur vapor pressure. The structure and surface composition of the synthesized films were characterized by grazing incidence X-ray diffraction and X-ray photoelectron spectroscopy. The films have rhombohedral 3R-NbS₂ structure and are nearly stoichiometric. The optical bandgaps of ultrathin NbS₂ samples were determined from ultraviolet–visible–near–infrared spectrometry to be in the range of ~0.43 to ~0.90 eV and indirect. This implies that the ultrathin NbS₂ film is semiconducting and differs from the metallic nature of bulk NbS₂. The Raman shifts show distinct Raman active modes that depend on film thickness. The simple growth method developed can be applied to other TMDCs in which the metal has a high oxide heat of formation.

1. INTRODUCTION

Bulk crystals of transition metal dichalcogenides (TMDCs) have been studied for decades.^{1,2} Bulk NbS₂ is known for its superconductivity at low temperature.² A TMDC consists of a stacking of weakly interacting two-dimensional (2D) MX₂S (one layer of M sandwiched between two layers of X, or X–M–X) where M is a transition metal from groups IV, V, or VI and X is a chalcogen atom from S, Se, or Te. The 2D layered structure of MX₂S has gained renewed interest after the intense worldwide study of two-dimensional graphene.³ In contrast to the graphene layer, the bandgaps of several 2D TMDCs are in the range of 1–2 eV, several of which are direct.^{4,5} These open up opportunities for new nanoelectronic,⁶ optoelectronic,⁷ sensing, and energy storage devices.⁸ For example, a top-gated single layer MoS₂ transistor with ~10⁸ on/off conductance ratio⁹ and a two-layer MoS₂ field effect thin film transistor that can detect NO gas at the 190 ppt level have been demonstrated.¹⁰

There are two major routes to synthesize TMDCs, bottom-up and top-down. Top-down methods include mechanical or liquid exfoliation from bulk TMDC materials,¹¹ while bottom-up methods include chemical vapor deposition and hydrothermal synthesis.^{12,13} Among different combinations of MX₂, MoX₂ and WX₂ are semiconductors whereas NbX₂ and TaX₂ are metals.¹⁴ MoS₂ and WS₂ have been synthesized through chemical vapor methods or mechanical exfoliation, and their properties have been studied extensively in contrast to less reported NbS₂.^{15,16} The challenge in the synthesis of NbS₂ is the delicate balance of the structure and stoichiometry of the films. Despite the challenges, nanosheets with thicknesses

ranging from 20 to 200 nm have been reported.¹⁷ Hexagonal 2H-NbS₂ (stoichiometric or nonstoichiometric), rhombohedral 3R-NbS₂ (stoichiometric or nonstoichiometric), and trigonal 1T-NbS₂ have been observed.^{1,17,18} The number, 1, 2, or 3 in front of R, H, or T indicates the number of layers in one unit cell. For different stoichiometric NbS₂ the corresponding morphologies differ. Various forms of NbS₂ including platelets,¹⁹ thin films,²⁰ nanobelt arrays,²¹ nanowires,^{14,22} nanoflakes,²³ and nanocables²⁴ have been synthesized using either physical or chemical routes.

Why is it challenging to synthesize NbS₂ films? In the synthesis of 2D WS₂ and few layer thick WS₂ triangular flakes, one starts with WO₃ that reacts with low pressure sulfur (slightly above the melting temperature of S, 115 °C) through 7S + 2WO₃ → 2WS₂ + 3SO₂ at ~900 °C.²⁵ Or one can react pure W and Mo films with low pressure sulfur (sulfur powders heated slightly above 100 °C) while the substrate is held at 750 °C²⁶ and 800 °C²⁷ to form WS₂ and MoS₂, respectively. However, these recipes do not work for the synthesis of NbS₂ films partly due to the fact that there is no NbO₃ and the Nb reacts with oxygen and forms stable Nb₂O₅ or NbO₂. The Nb₂O₅ and NbO₂ have higher heat of formation energy of ~–380 kJ/mol and ~–395 kJ/mol, respectively,²⁸ as compared with WO₃ (~–279 kJ/mol) or MoO₃ (~–248 kJ/mol). This means that one needs a higher sulfur pressure of up to 6 atm² and high temperature (>750 °C) to grow bulk NbS₂ single

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crystals. For NbS₂ thin films, the control of layer thickness and lateral size remains a challenge.

In this paper we report the first synthesis of ultrathin 3R-NbS₂ films from sputter deposited ultrathin Nb films on both thermal oxide covered Si wafers and quartz substrates. The ultrathin Nb film and sulfur powder were held at 850 °C during reaction. At this high temperature, the sulfur pressure is higher than 1 atm and the sulfur vapor reacts with the ultrathin Nb film to form an ultrathin NbS₂ film. This growth method is advantageous in that the NbS₂ thickness can be controlled by the starting Nb film thickness and the synthesis time is only about 30 min. The morphological, structural, compositional, vibrational, and optical properties were studied by scanning electron microscopy (SEM), atomic force microscopy (AFM), grazing incidence X-ray diffraction (GIXRD), X-ray photoelectron spectroscopy (XPS), Raman scattering, and ultraviolet–visible–near infrared (UV–vis–NIR) transmission and reflection.

2. EXPERIMENTAL SECTION

The Nb films of 2, 5, 10, 20, and 1000 nm thick were deposited by dc magnetron sputter deposition on 285 nm thick Si dioxide covered single crystal Si(001) substrates with low resistivities of 0.001–0.005 ohm cm. The 1000 nm thick Nb was used for thickness calibration. For UV–vis–NIR measurements 10 nm thick Nb samples were deposited on quartz substrates. The base pressure of the sputter chamber was $\sim 7.5 \times 10^{-7}$ Torr. The Ar gas flow rate was controlled at 2.01 sccm, the working pressure of Ar was set to 2.3 mTorr, and the power was set to 50 W (for 1000 nm thick Nb sample, the power was set to 200 W). The Nb target (99.95% purity) was in the form of a 3 in. round disk, and the distance from the target surface to the center of the substrate was ~ 15 cm. The deposition rate was ~ 3.5 nm/min, calibrated from the cross sectional image obtained from field emission scanning electron microscopy (SEM).

The Nb films with various thickness deposited on SiO₂/Si or quartz substrates were placed in a quartz boat (100 × 45 × 20 mm) positioned at the center of a 30 in. long quartz tube with an inside/outside diameter of 55/59 mm. This quartz tube was placed inside a one zone furnace. See Figure 1. Another quartz boat (50 × 45 × 20 mm) housing the 99.98% pure sulfur powder (8–10 g) was placed adjacently about 1 cm from the boat containing Nb/SiO₂/Si substrates. The quartz tube was purged with a high purity (99.99%) Ar gas with a flow rate of

950 sccm entering from the end closer to the sulfur boat, as indicated in the schematic. After 20 min of Ar gas purging at 950 sccm, the flow rate was reduced to 200 sccm instantaneously while both quartz boats were gradually heated up from room temperature to 850 °C within the furnace in about 80 min. The temperature was measured using a type K thermocouple. See Figure 1 for the location of thermocouple wires. The temperature was accurate to within ± 5 °C of a targeted temperature. The boats were kept at 850 °C for 30 min before the furnace filament current was reduced to zero over 5–6 min. The quartz tube was cooled down to room temperature in about 120 min. Argon gas purging was continuous during the entire heating up and cooling down processes. The temperature ramping was managed using a Eurotherm 2116 PID programmable temperature controller attached to the furnace. The furnace and Ar gas handling lines were placed inside a venting hood.

The surface of each synthesized sample was imaged via AFM (PSIA XE100) in noncontact mode. The AFM tip (HI-RES-C14/CR-AU) has a radius of ~ 1 nm with a force constant of 5 N/m and a resonant frequency of 160 kHz. The top views of synthesized samples were imaged by a field emission SEM (Zeiss Supra 55 FE-SEM).

GIXRD theta–2theta (θ – 2θ) scans of synthesized samples were collected using a PanAlytical X'Pert Pro diffractometer to characterize the atomic structure and average grain size of the NbS₂ films. A parallel X-ray beam generated from a parabolic mirror with a wavelength of 1.5405 Å was incident on the sample at a fixed 1.5° grazing incident angle (ω). During the GIXRD scan, ω was fixed at 1.5° while 2θ was varied. A point detector was used to scan the diffracted intensity 2θ away from the substrate surface in the scattering plane that contains the incident X-ray and surface normal. The scanning step size of the detector used was 0.013° with a counting time of 0.25 s at each step.

XPS was used to determine the composition near the surface of the sample. The nearly monochromatic X-ray Mg K source (PHI model 04-151) had a primary energy of 1253.6 eV. The X-ray source was operated at 270 W with a 10 kV high-voltage bias and a 27 mA emission current. A double pass cylindrical mirror energy analyzer (PHI model 15-255G) was used to detect the emitted electrons from the surface. A high-resolution spectrum was averaged from 40 repeated scans at a passing energy of 50 eV. The resolution of the analyzer at this passing energy is about 0.7 eV. The binding energy of C 1s of 284.8 eV was chosen as the reference for energy scale calibration. A 0.08 eV energy step size was used to scan the Nb and S peaks in order to provide a good relative resolution between peaks.

Raman spectra revealing the vibrational modes were collected using a Witec Alpha300 R confocal Raman microscope. The laser wavelength and power used in the collection of Raman spectra were 532.1 nm and 17 mW, respectively. A 100× objective lens produced a spot size of ~ 721 nm ($= 1.22 \times$ wavelength/numerical aperture of 0.9 for the 100× objective lens). The spectral resolution and step size used in Raman spectra collection were each 0.02 cm^{−1}.

UV–vis–NIR transmission and reflectance spectra were collected to determine the optical band gap of the ultrathin NbS₂ films on quartz substrates. Spectra were obtained using a PerkinElmer Lambda 950 UV–vis–NIR spectrometer. The transmission spectra were obtained in air with slides held normal to the incident light beam and corrected for the quartz

Figure 1. Schematic (not to scale) of the experimental setup for the synthesis of NbS₂ films. The larger quartz boat containing sputter-deposited Nb films on SiO₂ on Si(001) substrates and the smaller quartz boat containing sulfur powder are placed inside a one zone furnace. Thermocouple wires are placed near the center of the furnace. Argon gas flows from the sulfur boat side to the Nb film side as indicated by the blue arrows.

Figure 2. SEM top view images of synthesized NbS_2 films starting from (a) 10 nm and (b) 1000 nm thick Nb films. The inset in (b) shows one NbS_2 island. AFM images of synthesized NbS_2 films starting from (c) 10 nm and (d) 1000 nm thick Nb films. The corresponding height histograms are shown beneath each AFM image. Note that the height histogram describes the island height variation and its mean height is about twice the film thickness.

background. Specular reflectance spectra were obtained at a near-normal incidence angle of 6° .

3. RESULTS AND DISCUSSION

3.1. Morphology of Synthesized NbS_2 Films. Synthesized samples from Nb films of thicknesses 2, 5, 10, 20, and 1000 nm are labeled as S_2 , S_5 , S_{10} , S_{20} , and S_{1000} , respectively. The surface morphology of each sample was examined by SEM and AFM. SEM images of S_2 , S_5 , and S_{10} show island-like features (see Figure 2a for SEM top view of S_{10}). For S_{20} and S_{1000} the SEM images show shallower islands and plate-like islands, respectively. Figure 2b shows the SEM top view image of S_{1000} . It shows that most islands are hexagonally shaped and some islands are triangular or pentagonal in shape. The inset in Figure 2b shows a hexagonal plate-like island with its surface parallel to the substrate. The lateral size and thickness are ~ 500 nm and ~ 100 nm, respectively. The surface of each hexagonal

island is not always parallel to the substrate. Some hexagonal islands' surfaces are tilted away from the substrate surface.

AFM top view images corresponding to samples shown in Figures 2a and 2b are shown in Figures 2c and 2d, respectively. The small and large islands observed in the AFM images shown in Figure 2c and Figure 2d are consistent with those of the SEM images shown in Figure 2a and Figure 2b, respectively. One of the hexagonally shaped islands in Figure 2d is outlined by a yellow border, and its size is comparable to the one observed in the SEM image in Figure 2b. Height histograms are shown below each AFM image. The histogram of S_{10} has a height distribution of islands ranging from a few nanometers up to 40 nm with a mean height of ~ 20 nm, which is about twice the original 10 nm Nb thickness. All other histograms of thinner NbS_2 samples (S_2 , S_5 , and S_{20}) also show that the mean height of the NbS_2 islands is about twice the thickness of the original Nb film before sulfurization. The synthesized films are

Table 1. Bragg Peak Position, Orientation (in Parentheses), and Average Grain Size of Synthesized NbS₂ Films from Nb Films of Various Thicknesses as Determined from GIXRD Peaks and Surface Roughness Parameters Analyzed from AFM Images

sample	GIXRD		AFM		
	NbS ₂ film (orientation); 2 θ peak position (deg)	av grain size (nm)	surface width (nm)	correlation length (nm)	roughness exponent
5 nm Nb on SiO ₂ /Si(001)	(110); 38.614	5.5 $\pm$ 0.1			
synthesized films					
S ₂	(003); 14.851 (006); 29.964	7.2 $\pm$ 0.1	2.85 $\pm$ 0.11	48.6 $\pm$ 1.2	0.82 $\pm$ 0.01
S ₅	(003); 14.851 (006); 29.964	12.8 $\pm$ 0.2	3.84 $\pm$ 0.12	66.4 $\pm$ 1.5	0.81 $\pm$ 0.01
S ₁₀	(003); 14.852 (006); 29.964	19.6 $\pm$ 0.2	5.26 $\pm$ 0.15	68.5 $\pm$ 1.7	0.75 $\pm$ 0.02
S ₂₀	(003); 14.852 (006); 29.964 (104); 37.030 (107); 47.585	38.9 $\pm$ 0.3	6.47 $\pm$ 0.18	76.4 $\pm$ 2.1	0.72 $\pm$ 0.02
S ₁₀₀₀	NbS ₂ (003); 14.852 (006); 29.963 (101); 31.332 (012); 32.542 (104); 37.030 (015); 40.102° (107); 47.485 Nb ₂ O ₅ (001); 22.592 (180); 28.398	85.4 $\pm$ 0.4	31.9 $\pm$ 0.56	479.3 $\pm$ 3.5	0.86 $\pm$ 0.01

thicker than the initial Nb films due to the incorporation of sulfur. The histogram of S₁₀₀₀ shows that the height distribution is much wider, ranging from a few nanometers to over 100 nm. Note that the height histogram for the thicker film such as S₁₀₀₀ is not the absolute height of the S₁₀₀₀ but the height variation near the surface of the film. AFM line scans across a hexagon show that the difference between the top and bottom of a hexagon is $\sim$ 100 nm. For the thicker sample S₁₀₀₀, a cross-sectional view of the sample has been imaged by SEM. (The obtained image is not presented in the manuscript.) The image supports that the original Nb thickness increases to approximately twice the thickness after sulfurization. All the synthesized films are thicker than the initial Nb films due to the incorporation of sulfur.

Table 1 lists the surface roughness parameters including surface width ω (vertical root-mean-square roughness), lateral correlation length ξ , and local roughness exponent α extracted from height–height correlation analysis^{29,30} of AFM images of S₂, S₅, S₁₀, S₂₀, and S₁₀₀₀. The surface width and lateral correlation length increase about 1 order of magnitude as the film thickness increases. The lateral correlation length size is about 48 nm for S₂ and increases to $\sim$ 76 nm for S₂₀. The largest lateral correlation length is $\sim$ 480 nm for S₁₀₀₀. It is of the same order of magnitude as the $\sim$ 500 nm plate-like islands observed in the SEM image in Figure 2b and AFM image in Figure 2d. As larger α values indicate a smoother local surface, the decreasing value of the roughness exponent as film thickness increases implies that local roughness increases except for S₁₀₀₀.

3.2. Structures of Synthesized NbS₂ Films. Figure 3 shows GIXRD theta vs two theta spectra measured from one 5 nm thick pure Nb film before synthesis and synthesized films S₂, S₅, S₁₀, S₂₀, and S₁₀₀₀. Table 1 lists the measured Bragg

Figure 3. Grazing incidence X-ray diffraction spectra of 5 nm thick pure Nb film, and synthesized NbS₂ films starting from 2, 5, 10, 20, and 1000 nm thick Nb films. The NbS₂ spectra match with the 3R-phase (JCPDS #38-1367).

angles. The pure Nb film exhibits one peak at 38.614°. Nb has a lattice constant of 0.330 nm, thus this single peak is identified as the (110) plane from Bragg's law. Nb has a bcc structure, and the lowest surface energy plane is (110). For S₂, S₅, and S₁₀, two peaks are observed at 14.851° and 29.964° that correspond to Bragg angles from (003) and (006) planes of NbS₂ using a lattice constant $c = 1.7867$ nm in the calculation of Bragg angles. For S₂₀ additional peaks at 37.030° and 47.585° appear. For S₁₀₀₀, there are additional peaks observed at 31.332°, 32.542°, 37.030°, 40.102°, and 47.485°. These measured peak

positions correspond to calculated Bragg angles from (101), (012), (104), (015), and (107) planes of NbS_2 if lattice constants $a = b = 0.3335$ nm, $c = 1.7867$ nm, and $\alpha \neq \beta \neq \gamma$ of bulk rhombohedral 3R structure of NbS_2 are used. Based on the observed Bragg angles, we conclude that the synthesized films have a 3R NbS_2 phase (JCPDS #38-1367) with the (003) dominant orientation in the ultrathin film regime (from S_2 , S_5 , and S_{10}). For S_{20} the dominant Bragg peak changes from (003) to (104) and another peak (107) appears. For S_{1000} the dominant Bragg peak is (101) and additional peaks (012) and (015) appear.

For S_{1000} in addition to NbS_2 peaks the peaks at 22.592° and 28.398° appear. These correspond to Bragg peaks of (001) and (180) from Nb_2O_5 with the lattice constants $a = 0.6175$ nm, $b = 2.9170$ nm, $c = 0.3930$ nm, and $\alpha = \beta = \gamma = 90^\circ$ for an orthorhombic Nb_2O_5 structure.³¹ In all synthesized NbS_2 films there is no pure Nb(110) peak implying that all starting Nb films have been consumed in the synthesized NbS_2 films under our growth conditions.

Similar GIXRD spectra were obtained for a second set of samples synthesized from Nb films of various thicknesses grown on 300 nm thick SiO_2 on high resistivity Si(001) substrates as well as for a film synthesized from 10 nm thick Nb on a quartz substrate. We learn from these reproducible results that, when the starting Nb film thickness increases, the synthesized NbS_2 film becomes more polycrystalline and Nb oxides form under our growth conditions.

The average grain size of NbS_2 can be estimated from the full-width-at-half-maximum (fwhm) of a GIXRD peak. Grain sizes estimated from the (003) peaks of S_2 , S_5 , S_{10} , S_{20} , and S_{1000} using the Scherrer formula³² are listed in Table 1. Size increases with film thickness. The grain sizes in the NbS_2 films are about a factor of 2 to 3 larger than the original Nb film thickness when the Nb film is less than 20 nm thick. As mentioned previously this is because of the sulfur incorporation during the formation of the 3R- NbS_2 structure. In addition, the NbS_2 films possess islands and are not smooth films. For S_{1000} the grain size is about 85 nm, implying that the average grain size is much smaller than the plate-like structures shown in Figures 2b and 2d by SEM and AFM, respectively.

Judging from our GIXRD, S_2 , S_5 , and S_{10} have a dominant orientation direction [003] approximately perpendicular to the substrate ($\sim 6^\circ$ from substrate normal = theta angle $- 1.5^\circ$ X-ray grazing incident angle), but S_{20} and S_{1000} have dominant grain orientations approximately in the [104] and [101] directions, respectively. This change of dominant orientation is consistent with the morphological change. For example, the SEM image in Figure 2a has a smooth morphology but the plate-like islands in Figure 2b are tilted in all directions. Some plates are almost perpendicular to the substrate similar to those observed by Ge et al.¹⁷ These authors observed that the orientation of NbS_2 nanosheets depended on the substrate used. For example, vertical standing NbS_2 nanosheets were grown on Si or SiO_2 substrates but parallel NbS_2 nanosheets were grown on a transferred graphene surface on SiO_2/Si substrates. In our sample S_{1000} the plate-like islands shown in Figure 2b have a wide range of tilt angles relative to the substrate.

3.3. Near Surface Composition of Synthesized Ultrathin Film. Figure 4 shows an XPS spectrum of S_5 . Five peaks including Nb 3d_{5/2}, Nb 3d_{3/2}, S 2p_{3/2}, S 2p_{1/2}, and O 1s are observed in the binding energy range from 0 to 550 eV. The left inset provides a closer look at the Nb 3d_{5/2} and Nb 3d_{3/2}

Figure 4. X-ray photoelectron spectroscopy spectrum of the synthesized NbS_2 film starting with a 5 nm thick Nb film. The upper left and upper right insets show Nb 3d and S 2p spin-orbit splittings, respectively. Origin peak fits (red curves) using two Gaussian curves (blue curves) are shown under each peak.

peaks in the decreased range of 190 to 215 eV. The right inset shows the S 2p_{3/2} and S 2p_{1/2} peaks in the energy range of 150 to 170 eV. Quantitative composition of Nb and S near the sample surface can be calculated from the ratio of the Nb 3d_{5/2} peak area to the S 2p (including both S 2p_{1/2} and S 2p_{3/2}) peak area. The XPS background intensity of each peak was first subtracted using a Shirley background subtraction, and then the peak area was fitted using a Gaussian intensity distribution. The peak area and fitting error were obtained from the Gaussian fit. The peak positions for the Nb 3d_{5/2}, Nb 3d_{3/2}, S 2p_{3/2}, S 2p_{1/2}, and O 1s peaks are 204.2, 206.9, 161.3, 162.2, and 532.4 eV, respectively. The Nb 3d_{5/2} and S 2p peak areas are 331 and 227 in arbitrary units, respectively. The ratio Nb/S = (area of Nb 3d_{5/2}/S_{Nb})/(area of S 2p/S_S), where S_{Nb} = 1 and S_S = 0.35 are sensitivity factors for Nb 3d_{5/2} and S 2p (including both S 2p_{3/2} and S 2p_{1/2}), respectively. The calculated Nb to S ratio is 1.021/2.00. In addition to Nb and S, about 10% oxygen also exists in the near-surface region. Similar analyses of XPS spectra measured from films S_2 , S_{10} , S_{20} , and S_{1000} have also been carried out (shown in Figure S1). The Nb to S ratios determined from films S_2 , S_{10} , S_{20} , and S_{1000} are 1.017/2.00, 1.031/2.00, 1.034/2.00, and 1.045/2.00, respectively. These XPS results indicate that the near surface chemical composition of synthesized films is consistent with the stoichiometry of NbS_2 . We note that the XPS spectrum shown in Figure 4 has an oxygen peak that is common for a sample exposed to air. The oxygen is less than 10% of the surface atomic composition. Compared to iodine containing NbS_2 nanowires synthesized from catalyzed iodine(I) transport reaction involving C_{60} where the XPS shows an atomic ratio of 1:2.05:0.41 for Nb:S:I,²² our samples do not have iodine.

The spin-orbit splitting between the observed Nb 3d_{5/2} and Nb 3d_{3/2} XPS peaks with binding energies of 204.2 and 206.9 eV, respectively, is 2.7 eV. This value is comparable to the observed 2.8 eV splitting between 203.5 and 206.3 eV binding energies from NbS_2 powders sintered at 900 °C.³³ The observed 0.9 eV spin-orbit splitting between the binding energies of 161.3 and 162.2 eV for the S 2p_{3/2} and S 2p_{1/2} peaks, respectively, is also comparable with the observed 0.8 eV

splitting between the 161.3 and 162.1 eV binding energies from NbS₂ nanowires.²²

3.4. Optical Bandgap of Ultrathin NbS₂ Film on Quartz. UV–vis–NIR transmission and specular reflectance spectra were collected for the ultrathin NbS₂ film synthesized from the 10 nm thick Nb film on a quartz substrate. The transmission spectrum was corrected for quartz background (measured from a bare quartz substrate annealed at 850 °C without any deposited Nb). Figure 5a shows the total

Figure 5. (a) UV–vis–NIR transmittance (blue curve) and reflectance (red dashed curve) vs wavelength spectrum of the NbS₂ film, S₁₀ measured at room temperature (the NbS₂ film was synthesized from a 10 nm thick Nb film on a quartz substrate). (b) The calculated absorptivity coefficient from the transmission and reflectance data. (c) Tauc plot of $(\alpha h\nu)^{1/2}$ vs $h\nu$ for S₁₀. The indirect optical bandgap was calculated by fitting the linear region from 1.1 to 1.7 eV (open black circles, every 25th data point is plotted) yielding an intercept of 0.90 ± 0.02 eV.

transmittance (blue curve) and reflectance (red dashed curve) vs wavelength. The transmittance spectrum shows high transmittance in the NIR range that drops as the wavelength decreases toward the UV–vis–NIR wavelength range, with a minimum around 300 nm. Figure 5b shows the absorption coefficient vs photon energy as calculated from the transmission and reflectance spectra.³⁴ The resulting curve for the absorption

coefficient, α of the NbS₂ film shows a sharp peak around 4 eV (~ 300 nm wavelength). The optical bandgap of the NbS₂ film was determined from the experimental UV–vis–NIR absorption spectra via the Tauc method³⁵ by extrapolating the linear portion of the $(\alpha h\nu)^{1/2}$ vs $h\nu$ plot to the intercept, where $h\nu$ is the photon energy and the exponent 1/2 indicates an indirect optical bandgap. Figure 5c shows the Tauc analysis plot for the NbS₂ film synthesized from 10 nm thick Nb on a quartz substrate. The plot of $(\alpha h\nu)^{1/2}$ vs $h\nu$ shows a linear region over the range of 1.1 to 1.7 eV and was fit by a least-squares regression resulting in a value for the indirect optical bandgap of 0.90 ± 0.02 eV. In a separate experiment the transmission and reflection spectra of an ultrathin metallic Nb film were measured using a UV–vis–NIR spectrometer. The spectra have finite transmission and reflection, but the values are flat and as a result no optical bandgap can be extracted using the Tauc plot. We have performed similar UV–vis–NIR experiments for samples S₂, S₅, S₂₀, and S₁₀₀₀. The UV–vis–NIR plots are shown in Figures S2, S3, S4, and S5. The bandgaps obtained from all ultrathin samples S₂, S₅, S₁₀, and S₂₀ were ~ 0.44 eV, ~ 0.63 eV, ~ 0.90 eV, and ~ 0.43 eV respectively. For the S₁₀₀₀ sample, it was opaque in the wavelength used. So only the reflectance spectrum was obtained, and band gap determination using Tauc plot analysis was not possible.

Our observed finite optical bandgaps for the ultrathin NbS₂ films imply a nonmetallic behavior in contrast to the bulk NbS₂, which is metallic. Literature reports that the optical absorption measurement of single crystal NbS₂ flakes grown by chemical vapor transport using iodine as the transport agent shows both indirect (1.49 eV) and direct transitions (1.56 eV).³⁶ The lower optical bandgap values extracted from our data may be related to the different thicknesses of samples used or different growth methods that may lead to different stoichiometry. A recent temperature dependent conductivity study of 58 and 195 nm thick NbS₂ nanoflakes shows that their conductivity decreases as the temperature decreases from 300 to 180 K.²³ This is consistent with temperature dependent behavior of conductivity exhibited by semiconductors. The absolute conductivity value is in the range of sub tens (58 nm thick flakes) and tens (195 nm thick flakes) of $\Omega^{-1} \text{ cm}^{-1}$. The low conductivity is also consistent with what is expected for semiconductors.

3.5. Raman Shifts of Synthesized NbS₂ Films. Figure 6 shows Raman spectra measured for films S₂, S₅, S₁₀, S₂₀, and S₁₀₀₀. The S₂₀ spectrum has seven pronounced peaks. The peak positions calculated by Origin software are 183.50, 208.10, 265.40, 312.67, 332.96, 383.70, and 452.10 cm^{-1} and are listed in Table 2. The four highest of these peaks are identified as nondegenerate Raman active modes, E₁, E₂, A₁, and A₂, respectively.^{17,37} The coefficient of determination for the fit of these four peaks is ~ 0.99 . The peak A₁ is an active mode in which the two sulfur atoms displace out-of-phase with respect to each other but parallel to the *c*-axis, while the Nb atom is stationary. The *c*-axis is perpendicular to the substrate. See the inset in Figure 6. The E₁ mode is similar to the A₁ mode except that the two sulfur atoms move parallel to the surface. In the A₂ mode the Nb atom displaces along the *c*-axis direction and the two sulfur atoms displace in-phase in the *c*-axis direction but out-of-phase with the displacement of the Nb atom. The peak E₂ is an active mode in which two sulfur atoms displace in-phase parallel to the substrate but both out-of-phase with respect to the Nb atom's displacement, which is also parallel to the substrate.

Figure 6. Raman spectra of synthesized NbS₂ films from 2, 5, 10, 20, and 1000 nm thick Nb films. Vibrational modes E₁, E₂, A₁, and A₂ are labeled.

The spectrum measured for S₁₀ also has seven peaks, although the peak positions shift a couple of cm⁻¹ relative to those of S₂₀. See Table 2. Films S₂ and S₅ have E₁, E₂, A₁, and A₂ peaks, with the E₁ and E₂ peaks overlapping. For the film S₁₀₀₀, the A₁ and A₂ peaks remain but other peaks such as E₁ and E₂ overlap and one new broad peak appears around 145.10 cm⁻¹. Judging from all the NbS₂ spectra the A₁ peak always exists and its peak position shifts about 3 cm⁻¹ to lower frequency as the film thickness increases from S₂ to S₂₀. In addition to the shift of A₁, as the thickness increases, the A₂ mode has about a 9 cm⁻¹ shift toward higher frequency. The difference in the relative Raman shift between the A₁ peak and A₂ peak also increases from 55.9 to 68.4 cm⁻¹ as the ultrathin film thickness increases. This difference is about the same as the difference in Raman shift from few layer thick WS₂³⁸ but is about a factor of 2 larger than that from few layer thick MoS₂.³⁹ The A₁ and A₂ peak position shifts, or the difference in shifts between A₁ and A₂ peak positions, may be used as a guide for the thickness estimation of the ultrathin NbS₂ films.

The three highest Raman peak shifts occur for the E₂, A₁, and A₂ peaks as observed from spectra of both ultrathin (S₂, S₅, S₁₀,

S₂₀) and thin (S₁₀₀₀) NbS₂ films. This is consistent with the Raman peaks of NbS₂ films^{17,20,23} and single crystal^{37,40,41} reported in the literature to within a few cm⁻¹. See the bottom half of Table 2. Our observed lowest shift peak E₁ at 312.67 cm⁻¹ is about 20 to 30 cm⁻¹ higher than most reported values in the literature. For a 3R-Nb_{1+x}S₂ structure the extra *x* in Nb could be a nonzero value. Our XPS result indicates the extra *x* ≈ 0.02–0.03 near the surface. The slightly Nb richness could change the strong intralayer bonding of M–X and thus change the amount of Raman frequency shift.

The width of a Raman peak is related to the configuration of bonds in the film. A uniform bonding gives a narrower Raman peak. Our observed Raman peaks appear to be sharper than reported NbS₂ Raman peaks. Most of the FWHMs of our Raman peaks are in the range of 10 to 20 cm⁻¹. The lower end of 10 cm⁻¹ is similar to literature reported FWHMs of peaks from spectra taken of a few layers of WS₂³⁸ and MoS₂.³⁹

During the synthesis of NbS₂ in a non-UHV environment it is likely that Nb oxides in various combinations may form in the Nb films. The outermost oxide is usually Nb₂O₅. The reported Raman spectrum of bulk Nb₂O₅ shows peaks at 180, 205, and 263 cm⁻¹,⁴² and the Raman spectrum of powder Nb₂O₅ shows peaks at 181, 207, and 261 cm⁻¹.⁴³ Our observed peaks at approximately 204, 210, 208, and 201 for films S₅, S₁₀, S₂₀, and S₁₀₀₀ as well as our observed peaks around 185 and 183 cm⁻¹, and 268 and 265 cm⁻¹, for films S₁₀ and S₂₀ may be from Nb₂O₅. Our observed Raman peaks near 185 and 268 cm⁻¹ are within 10 cm⁻¹ of literature reported peak positions such as 191 and 258 cm⁻¹ from NbS₂ films exhibiting island-like features²⁰ and 266 cm⁻¹ from single crystal NbS₂⁴² that may also have Nb₂O₅.

Our observed broad peak around 145 cm⁻¹ for S₁₀₀₀ may be from NbO₂ since for single crystalline NbO₂ one of the reported Raman peaks is 138 cm⁻¹.⁴⁴ Among literature reports, Raman peaks at 150 and 158 cm⁻¹ have been observed by Nakashima⁴⁰ and McMullan,³⁷ respectively, both from single crystal NbS₂. See Table 2. McMullan stated that the peak at ~158 cm⁻¹ is likely due to an impurity or defect mode. Our lowest Raman peak of 145 cm⁻¹ appears to indicate that this mode only exists in thick films or bulk single crystals.

The last row in Table 2 lists the prediction of Bromley's model for NbS₂.³⁷ The Bromley model⁴⁵ was originally applied to MoS₂ assuming only nearest-neighbor interactions and a single layer of MoS₂. Because the force constants in MoS₂ were

Table 2. Raman Shift Peak Positions of Synthesized NbS₂ Films of Various Thicknesses and a Comparison with Raman Shifts Peaks from Other NbS₂ Experimental Works as Well as the Bromley Model

authors	samples	Raman modes and shift positions (cm ⁻¹)						
		defect	defect	defect	E ₁	E ₂	A ₁	A ₂
this work, synthesized films	S ₂				312.42	332.47	387.21	443.12
	S ₅		204.80		312.56	332.24	386.70	448.10
	S ₁₀	185.60	210.20	268.70	312.52	332.89	383.80	451.60
	S ₂₀	183.50	208.10	265.40	312.67	332.96	383.70	452.10
	S ₁₀₀₀	broad	201.40	broad	304.00	332.45	384.10	446.20
Huang et al., ²³ 2014	nanoflakes				290	330	386	459
Ge et al., ¹⁷ 2013	nanosheets 20–200 nm				~280	327	386	~450
Carmalt, ²⁰ 2004	island-like film		191	258		322	386	462
McMullan, ³⁷ 1983	single crystal	158			290 shoulder	330	386	458
Nakashima, ⁴⁰ 1982		150			300	329	382	
Onari, ⁴¹ 1979				266	281	325	382	
Bromley model, ⁴⁵ 1971					223	330		404

not known, one of the observed Raman peak frequencies was used as a normalization frequency. For MoS₂, the model predicted vibration frequency ratios $\omega_H^2(x,y):\omega_D^2(x,y):\omega_D^2(z)$ to be 0.6:1:1.5 for an ideal coordination geometry, where the H and D represent the homopolar and dipolar vibrations of the lattice, respectively. This prediction agrees reasonably with experimental observation of (286)²:(384)²:(466)² or 0.56:1:1.48 from MoS₂ if $\omega_D^2(x,y) = (384)^2$ was used as the normalization frequency.⁴⁶ However, for NbS₂ the frequencies predicted by the Bromley model are 223, 330, and 404 cm⁻¹ (listed in the last row of Table 2). These frequencies do not agree well with previous experimentally measured peaks³⁷ or our observed peaks. If we use experimental frequencies (332)²:(386)²:(450)² cm⁻¹ we obtain 0.74:1:1.36. More advanced lattice dynamic modeling is needed.

4. CONCLUSIONS

We have synthesized ultrathin NbS₂ films on amorphous SiO₂/Si and quartz substrates. The NbS₂ films were grown from sputter deposited ultrathin Nb films deposited on substrates and annealed under flowing Ar and vaporized sulfur at 850 °C in 30 min. The synthesized NbS₂ film is continuous across the entire surface, and the thickness can be controlled from the starting Nb film thickness. From the AFM morphology characterization the synthesized NbS₂ film is about two to three times thicker than the starting Nb film. This increase in film thickness is consistent with the grain size analysis from grazing angle X-ray diffraction. The film is polycrystalline with a rhombohedral 3R structure and a preferred (003) orientation with the *c*-axis (of lattice constant *c* = 1.7867 nm) approximately perpendicular to the substrate. The chemical composition ratio of Nb/S determined from XPS is 1.02/2.00 with a slightly Nb rich stoichiometry. The UV–vis–NIR spectra of ultrathin NbS₂ films show an indirect optical band gap in the range of ~0.43 to ~0.90 eV, implying that it is a semiconductor. Raman spectra taken of each sample show distinct active Raman modes. The A₁ Raman mode shifts to a lower frequency and the A₂ Raman mode shifts to a higher frequency as the NbS₂ film thickness increases. The difference in Raman shift is comparable with other TMDC layer materials such as MoS₂ and WS₂. Our growth methodology can be applied to synthesis of other TMDC materials where the metal has a high oxide heat of formation.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b04057.

XPS spectra and UV–vis–NIR plots for the synthesized NbS₂ films (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jatiskumar@gmail.com, dashj@rpi.edu.

Notes

The authors declare no competing financial interest.

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