

Strain controlled superconductivity in few-layer NbSe₂Cliff Chen, Protik Das, Ece Aytan, Weimin Zhou, Justin Horowitz,
Biswarup Satpati, A.A. Balandin, Roger K. Lake, and Peng WeiACS Appl. Mater. Interfaces, **Just Accepted Manuscript** • DOI: 10.1021/acsami.0c08804 • Publication Date (Web): 28 Jul 2020

Downloaded from pubs.acs.org on August 1, 2020

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.

Strain controlled superconductivity in few-layer NbSe₂

Cliff Chen¹, Protik Das², Ece Aytan², Weimin Zhou¹, Justin Horowitz¹, Biswarup Satpati³,
Alexander A. Balandin², Roger K. Lake² and Peng Wei^{1*}

1. Department of Physics and Astronomy, University of California, Riverside, CA 92521, United States

2. Department of Electrical and Computer Engineering, University of California, Riverside, CA 92521, United States

3. Surface Physics & Material Science Division, Saha Institute of Nuclear Physics, 1/AF Bidhannagar, Kolkata 700 064, India

*Correspondence to: peng.wei@ucr.edu

Abstract: The controlled tunability of superconductivity in low-dimensional materials may enable new quantum devices. Particularly in triplet or topological superconductors, tunneling devices such as Josephson junctions etc. can demonstrate exotic functionalities.¹ The tunnel barrier, an insulating or normal material layer separating two superconductors, is a key component for the junctions. Thin layers of NbSe₂ have been shown as a superconductor with strong spin orbit coupling,²⁻⁴ which can give rise to topological superconductivity if driven by a large magnetic exchange field.⁵⁻⁹ Here we demonstrate the superconductor-insulator transitions in epitaxially grown few-layer NbSe₂ with wafer-scale uniformity on insulating substrates. We provide the electrical transport, Raman spectroscopy, cross-sectional transmission electron microscopy, and X-ray diffraction characterizations of the insulating phase. We show that the superconductor-insulator transition is driven by strain, which also causes characteristic energy shifts of the Raman modes. Our observation paves the way for high quality heterojunction tunnel barriers to be seamlessly built into epitaxial NbSe₂ itself, thereby enabling highly scalable tunneling devices for superconductor-based quantum electronics.

Keywords: two-dimensional material, tunable superconductor, heterostructure material, strain effect at interface, superconducting devices

I. Introduction:

Imposing structural perturbations to thin layers of NbSe₂ can be used as a potential knob to control superconductivity. NbSe₂ is often found in its prismatic 2H phase, i.e. the superconducting phase, in devices fabricated from exfoliated thin crystals.^{2,4,10} Insulating NbSe₂ is rare,¹¹ although it has been recently demonstrated in the 1T phase of NbSe₂.¹² However, a controlled tuning in between the superconducting and insulating states of NbSe₂ has not yet been achieved. NbSe₂ thin layers are often either exfoliated or grown on another two-dimensional (2D) material such as graphene.^{3,13} Due to Van der Waals interaction, the coupling between the layer and the substrate is weak, and the substrate often does not play a major role in determining the electrical properties of NbSe₂.

II. Experimental Methods and Results:

We demonstrate the electrical properties of few-layer NbSe₂ grown using MBE on a non 2D material substrate, i.e. on sapphire. Because the growth is epitaxial, the sapphire substrate couples to the NbSe₂ layer. One evidence of such coupling is seen from the locked [210] crystalline directions between the substrate and the NbSe₂ layer as observed in situ by reflection high energy electron diffraction (RHEED) during the growth (Fig 1c). Ideally, NbSe₂ has a much smaller lattice constant ($a \sim 3.44 \text{ \AA}$)¹⁴ compared to that of the *c*-cut sapphire ($a \sim 4.76 \text{ \AA}$), and one would not expect the growth to be epitaxial. However, by considering the 3×3 unit cells of NbSe₂ and the 2×2 unit cells of the *c*-cut sapphires surface, the two crystals do match with each other and the mismatch is only $\sim 7.8\%$. Such superlattice cell matching has been previously reported in the epitaxial growth of high quality transition-metal dichalcogenides (TMD) thin layers, for example WSe₂, on sapphire substrate.¹⁵ Notably, when considering the superlattice matching, the *c*-cut sapphire substrate imposes a planar compressive strain to NbSe₂. Similar heterogeneous growth,

1
2
3 i.e. growing a material epitaxially on top of another one with drastically different properties, has
4 demonstrated many emerging physics phenomena. One example is the epitaxial growth of Fe on
5 GaAs(001) giving rise to the Fe/GaAs(001) heterostructures, in which tunneling anisotropic
6 magnetoresistance and spin-orbit proximity effects have been shown.^{16,17}
7
8
9
10
11

12 By controlling the growth temperatures, we obtain the NbSe₂ layers with two distinctive
13 phases: one being a superconductor and the other one being an insulator (or semiconductor).
14 Because our substrate is sapphire, we are able to carry out the electrical transport characterizations
15 of both phases. We confirm that the insulating (or semiconducting) NbSe₂ has a gapped Fermi
16 surface and also demonstrates a shift of the Raman peaks with respect to the standard 2H-NbSe₂
17 Raman modes. It is known that the Raman peak shift often indicates a hardening or softening of
18 the lattice vibration modes, which may result from lattice strain effect. Using selective area
19 diffraction (SAD) based on cross-sectional transmission electron microscopy (TEM) and X-ray
20 diffraction (XRD), we show a lateral compression and a vertical expansion of the NbSe₂ lattice -
21 agreeing well with the Raman results. Our findings provide insight to the transition between the
22 insulating and superconducting electronic properties of the two phases.
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37

38 The quality of our epitaxially grown NbSe₂, including crystal symmetry and epitaxial
39 orientation, is confirmed by in situ RHEED experiment (Fig. 1a-1c). A 0.5 monolayer (ML) NbSe₂
40 seed, which does not completely cover the sapphire substrate, is used to facilitate the growth (see
41 SI). The six-fold rotational symmetry of the grown layer is confirmed by a planar rotation of the
42 RHEED electron beam from [210] to [110] directions (Fig. 1c). It is also clear that the crystalline
43 orientations of NbSe₂ and sapphire are locked as [210]_{NbSe₂} // [210]_{sapphire} (Fig. 1a-1c), which infers
44 that there is an interaction between NbSe₂ and the substrate, and thus would lead to strain effect.
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 The growth is proved to be layer-by-layer. Each monolayer of NbSe₂ is clearly defined as
4 shown in the TEM image (Fig 1d, 5ML NbSe₂). According to the scale bar of the TEM image, Fig
5 1d also shows that each NbSe₂ monolayer extends continuously over a large distance. It thus
6 suggests that atomically thin NbSe₂ on sapphire is achievable using MBE. The wafer-scale
7 coverage of NbSe₂ is further confirmed by both XRD and atomic force microscopy (AFM) (Fig.
8 2a and 2b). The quality of NbSe₂ is demonstrated by a set of characteristic XRD diffraction peaks
9 (Fig. 2a). AFM shows that the grown NbSe₂ layer has a wafer-scale coverage over the substrate
10 (Fig 2b). The terrace-like feature in Fig 2b indicates that the NbSe₂ layer follows the atomic
11 terraces of sapphire, which agrees with the uniform island-free growth of NbSe₂. The crystalline
12 quality of the NbSe₂ samples, down to a few MLs, is also confirmed by electron diffractions carried
13 out locally in a cross-sectional region of NbSe₂ using SAD (Fig 2c). The NbSe₂ diffraction pattern
14 is distinct from the substrate pattern with the (002) series diffraction spots aligned with the (006)
15 series of the sapphire substrate. The spatially resolved energy dispersive X-ray spectroscopy (EDX)
16 line scan shows no element segregations in the layer and a clear interface with the substrate. The
17 EDX also shows no contamination in the NbSe₂ layer, and an atomic ratio ~ 1:2 for Nb:Se (Fig
18 S2b in SI). Further, using atomically resolved scanning transmission electron microscopy (STEM),
19 the relative arrangement of Nb and Se atoms is clearly observed (Fig S1c in SI). The above studies
20 confirm that stoichiometric NbSe₂ layers have been grown.

21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45 A systematic tuning of the superconductivity is achieved by controlling the growth
46 condition of in NbSe₂ (Fig. 3a). Both increasing the growth temperature and decreasing the layer
47 thickness cause a decrease of T_C (Fig. 3b). However, as the growth temperature increases, even in
48 thick samples, the sample resistance starts to develop a sharp upturn at low temperature (Fig. 3b
49 inset). To clarify the origin of the resistance upturn, we increase the growth temperature to 600 °C,
50
51
52
53
54
55
56
57
58
59
60

1
2
3 which gives rise to an insulating (or semiconducting) NbSe₂ sample in the full temperature range
4 (Fig. 3a blue). A plot of $\ln(R)$ vs. T^{-1} is used to validate the origin of the insulating behavior. We
5
6 find that a linear fit well describes the $\ln(R)$ vs. T^{-1} plot (Fig. 3a inset) in a wide temperature
7
8 range (13 K and above), which is not the case if a variable range hopping model is adopted (Fig
9
10 S4 in SI). Thus, the insulating behavior is not due to localization effects caused by defects. It
11
12 confirms a gapped Fermi surface with the conductivity given by $\sigma \sim e^{-\frac{E_0}{k_B T}}$, where the activation
13
14 energy determined to be $\frac{E_0}{k_B} \sim 6.7$ K. Interestingly, we see little changes on crystal structure between
15
16 the superconducting and insulating samples (Fig S2a). Both have similar lattice constants and the
17
18 same hexagonal rotation symmetry (Fig S2a). Further, the insulating sample (grown at $T_g \sim 600$
19
20 °C) has even better sample quality (Fig S2a and Fig S3). Therefore, the insulating behavior is not
21
22 due to the degradation of the NbSe₂ sample when growing at 600 °C.
23
24
25
26
27
28
29

30 Although RHEED does not show visible changes, the difference between the two types of
31
32 NbSe₂ samples is visible in Raman spectroscopy, which is known to be sensitive to various
33
34 structural transitions in a wide range of materials.^{18,19} First, we compare the Raman spectrum of a
35
36 5 ML superconducting sample to that of a bulk NbSe₂ flake in Fig 3c. The two spectra resemble
37
38 each other by both showing the A_{1g}, E¹_{2g} and the soft mode peaks, which confirms the quality of
39
40 the MBE grown layer. Compared to bulk NbSe₂, it is clear that the E¹_{2g} peak of the MBE grown
41
42 NbSe₂ blue shifts to a higher wave number, while the A_{1g} peak red shifts to a lower wave number
43
44 (Fig 3c). The nature of the E¹_{2g} and A_{1g} vibration modes is further confirmed by polarized Raman
45
46 spectroscopy (Fig 3d), in which the *p*-polarization turns off the A_{1g} peak while maintaining the
47
48 E¹_{2g} peak, consistent with prior reports in 2H-NbSe₂.¹⁰ The blue shift of E¹_{2g} or the red shift of A_{1g}
49
50 is related to the hardening or softening of phonons, which could be a result of the change of lattice
51
52
53
54
55
56
57
58
59
60

1
2
3 parameters due to strain.²⁰ It is also known that the hardening of a phonon mode is often
4 unfavorable to superconductivity.
5
6

7
8 To further understand the change of the Raman modes, we carried out a series of Raman
9 spectroscopy experiments with a focus on the shift of the E_{2g}^1 and A_{1g} peaks (Fig 4a). The
10 measurement is done in a set of NbSe₂ samples (ranging from superconducting to insulating) that
11 are grown at difference temperatures. The corresponding resistance as a function of temperature is
12 plotted in Fig 3a. A two-peak Gaussian fit is adopted to identify the E_{2g}^1 and A_{1g} peak locations
13 (Fig 4a). A clear increase of the E_{2g}^1 peak, from 245 cm⁻¹ to 260 cm⁻¹, is observed, which
14 corresponds to the transition from superconducting to insulating in NbSe₂. At the same time, the
15 A_{1g} peak decreases. The validity of the comparison is guaranteed by the aligned sapphire substrate
16 Raman peak at 418 cm⁻¹. It has been shown that the E_{2g}^1 mode represents the vibration of atoms
17 within a monolayer layer of NbSe₂, and the A_{1g} mode represents the vibration perpendicular to the
18 monolayer.²¹ The opposite shift of the E_{2g}^1 and A_{1g} modes could reflect different strain effects
19 parallel and perpendicular to the monolayer. Because the (001) plane of NbSe₂ is in parallel to the
20 (001) plane of sapphire, the shift of E_{2g}^1 could be due to the strain effect within the NbSe₂
21 monolayer. To confirm it, we carried our SAD in both the superconducting sample (growth
22 temperature $T_g \sim 400$ °C) and the insulating sample (growth temperature $T_g \sim 600$ °C). Fig 4b
23 shows a result of the comparison of SAD. There is a clear shift of the NbSe₂ ($\underline{1}22$) SAD diffraction
24 spot. The validity of the comparison is based on the well aligned NbSe₂ (002) and Al₂O₃ ($\underline{1}02$)
25 SAD diffraction spots by knowing that the NbSe₂ (002) spot is along the same direction as the
26 Al₂O₃ (006) spot (Fig 2c). Comparing the insulating sample ($T_g \sim 600$ °C) with the
27 superconducting sample ($T_g \sim 400$ °C), one can see that the NbSe₂ ($\underline{1}22$) SAD spot moves away
28 in the k -space, which indicates a planar compression of the crystal lattice for the insulating sample.
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 Furthermore, to accurately determine the change of lattice constants along the c -axis
4 direction, we carried out XRD measurements on both types of samples (Fig 4c). After aligning the
5 Al_2O_3 (006) peaks, one can see that the insulating sample ($T_g \sim 600$ °C) has a lower NbSe_2 (002)
6 peak, which proves the increased (or expanded) c -axis lattice constant. The planar compression
7 and out-of-plane expansion of the crystal lattice agrees with the Raman results, in which the E_{12g}^1
8 has a blue shift and A_{1g} has a red shift (Fig 4a). The planar lattice compression agrees with the
9 aforementioned lattice mismatch between NbSe_2 and the sapphire substrate when considering the
10 7.8% smaller sapphire supercell compared to that of NbSe_2 , which has also been shown in the
11 MBE growth of other TMD materials on sapphire.¹⁵ On the other hand, the compression of the
12 planar crystal lattice could also result in an increase of the c -axis lattice constant causing a red shift
13 to the A_{1g} mode that describes the out-of-plane lattice vibrations.
14
15
16
17
18
19
20
21
22
23
24
25
26
27

28 **III. Discussion:**

29
30 Although we only measured the phonon modes at large wave numbers, such as the E_{12g}^1
31 and A_{1g} , when the lattice is under strain, the phonon modes at low wave numbers will also be
32 modified. According to BCS theory,²² the electron-phonon coupling strength is weakened when
33 the stiffness of the lattice vibrations increases, which can be caused by a compressive strain.
34 Similar effect has been previously reported in other 2D materials such as MoS_2 .²³ Our observations
35 are in agreement with them, and suggest that strain could cause the reduced T_c and the switching-
36 off of superconductivity in our metallic NbSe_2 samples (Fig 3b inset). Interestingly, we only see
37 lattice compression within the monolayer plane, whereas the c -axis is expanded (Fig 4c). Therefore,
38 our results point out that the planar vibration modes play a more important role on
39 superconductivity in NbSe_2 .
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 According to SAD (Fig 4b) and RHEED (Fig 4b and Fig S2c in SI) results, no structural
4 phase differences are observed in between the superconducting and insulating samples. Previously,
5 it has been reported that 1T-NbSe₂ is a Mott insulator, which is obtained by growing NbSe₂ at a
6 higher substrate temperature.¹² Our density functional theory (DFT) calculations show that the
7 Raman activated modes are very different between 2H-NbSe₂ and 1T-NbSe₂ (Fig S4 in SI). Thus,
8 our Raman results in Fig 4a do not suggest that our insulating sample is 1T-NbSe₂. We infer that
9 the insulating behavior could be due to the modified electron correlations such as the charge
10 density wave (CDW) or the change of band structure in NbSe₂ as a result of strain, which is often
11 seen in TMD materials.²⁴

12
13
14 Our results show that strain can serve as an effective knob in tuning the superconducting
15 properties of NbSe₂, which has been shown hard to be achieved by other means such as carrier
16 density tuning.²⁵⁻²⁷ The semiconducting (or insulating) NbSe₂ could serve as a high-quality tunnel
17 barrier material with a good lattice match with the superconducting 2H-NbSe₂, thereby would
18 enable a range of superconducting tunneling devices to be seamlessly built into NbSe₂. Further,
19 the semiconducting (or insulating) NbSe₂ may allow gate-controlled insulator to superconductor
20 transitions. TMD semiconductors in their 2H phase, for example 2H-MoS₂, can become
21 superconducting once significant amount of charge carriers are injected into the material by
22 gating.²⁸ Because our observed semiconducting (or insulating) NbSe₂ is in its 2H phase,
23 superconductivity can potentially be turned on by a dielectric gate. It would thus enable switchable
24 superconducting devices. These may also suggest the potential realization of 2D planar tunneling
25 devices such as 2D Josephson junctions in NbSe₂, which has been predicted as a scalable platform
26 for topological superconductivity and the manipulation of Majorana zero modes for fault-tolerant
27 topological quantum computing.²⁹

IV. Conclusion:

The growth of few-layer NbSe₂ using MBE has the advantage of producing heterostructures with ultra-clean interfaces, which are crucial for delivering high quality proximitized materials.¹⁷ Because the grown NbSe₂ layers are very thin, interface effect dominates the electrical properties of the heterostructure. New phenomena due to various proximity effects, such as magnetic proximity effects, superconducting proximity effects and spin-orbit proximity effects, can emerge. For magnetic proximity effect, heterostructures between NbSe₂ and other materials with large magnetic exchange fields^{30,31} can be grown in-situ by MBE. The in-situ growth enables ultra-clean interface that is crucial for the induced exchange field, and such NbSe₂ heterostructures are promising candidates for topological superconductors. For spin-orbit proximity effect, heterostructures can be grown by combining NbSe₂ with other materials having strong spin-orbit coupling (SOC), for example TMD materials WTe₂, WSe₂ etc. NbSe₂ can acquire stronger SOC or an additional interface SOC, which can be further tuned by a dielectric gate thereby enabling new spintronic devices.

V. Methods:

Growth of the NbSe₂ thin films was carried out in an ultrahigh vacuum chamber with a base pressure of $\sim 5 \times 10^{-7}$ torr. The films were monitored in-situ throughout the growth by reflection high energy electron diffraction (RHEED) with a 7.5mW beam energy. Ex-situ Raman spectroscopy was carried out on uncapped films using a Horiba LabRam system. A 6mW, 532nm unpolarized excitation laser with a 100 μ m spot size was used to scan the films. Ex-situ x-ray diffraction was done using a PANalytical Empyrean Series 2 diffractometer with Cu K-Alpha1 line. Transport measurements were carried out in a homemade liquid helium probe. The sample was mounted inside the probe using pressed indium contacts, purged with He gas, and then cooled

1
2
3 in a liquid helium dewar. Temperature was controlled by adjusting the insertion height of the probe.
4
5 The temperatures below 4.2K were achieved by letting additional He gas condense inside the probe
6
7 followed by pumping to reduce the vapor pressure. A Stanford Research Systems lock-in amplifier
8
9 was used to measure the resistance of the films in a four-terminal configuration. The DFT
10
11 calculations were carried out within the Perdew-Burke-Ernzerhof (PBE) generalized gradient
12
13 approximation and the projected augmented wave (PAW) method as implemented in software
14
15 package VASP.^{32,33} The van der Waals (vdW) interactions were accounted for using Grimme's
16
17 DFT-D2 semi-empirical correction to the Kohn Sham energies.³⁴
18
19
20
21
22
23

24 **Acknowledgments:**

25
26 We acknowledge Krassimir N. Bozhilov and the Central Facility for Advanced Microscopy and
27
28 Microanalysis (CFAMM) at UCR for technical supports. The research is supported as part of the
29
30 Spins and Heat in Nanoscale Electronic Systems (SHINES), an Energy Frontier Research Center
31
32 funded by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES),
33
34 under Award # SC0012670 (A.A.B., R.K.L. and P.W.). C.C., W.Z., J.H. and P.W. acknowledge
35
36 the support of the startup fund from UC Riverside, and partly by the National Science Foundation
37
38 (NSF) QLCI-CG under Award #1937155. The DFT calculations used the Extreme Science and
39
40 Engineering Discovery Environment (XSEDE),³⁵ which is supported by the National Science
41
42 Foundation Grant No. ACI-1548562 and allocation ID TG-DMR130081.
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Figures and captions:

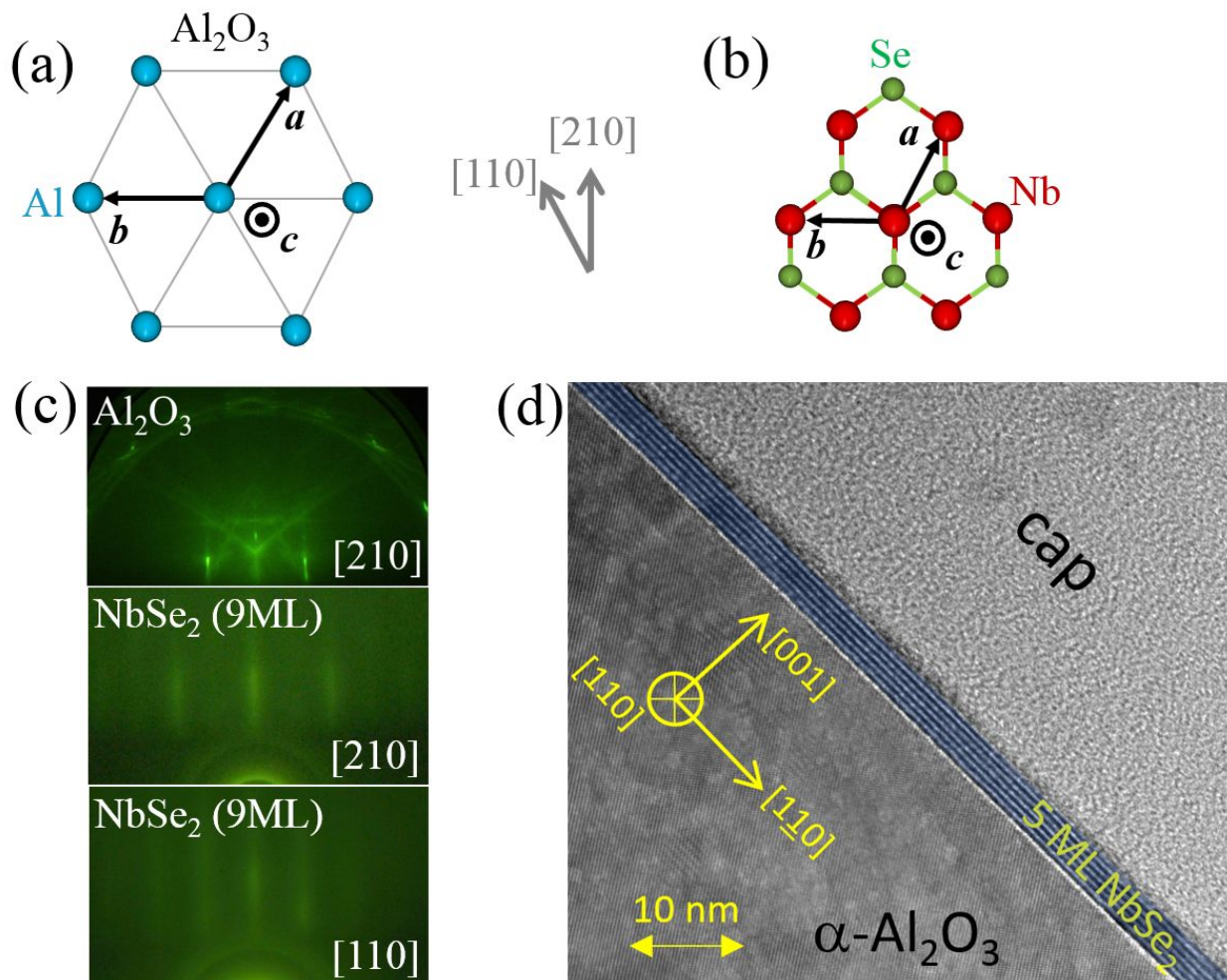


Fig. 1. (a) The schematic showing the Al atoms on sapphire (0001) surface. (b) The schematic of NbSe₂ surface and its epitaxial orientation with respect to the substrate in (a). (c) The RHEED patterns: sapphire substrate along $[210]$ direction (top), 9 ML NbSe₂ along $[210]$ direction (middle) and along $[110]$ direction (bottom). (d) TEM image of a 5 ML NbSe₂ sample. It can be clearly seen that each NbSe₂ monolayer extends continuously over a large scale.

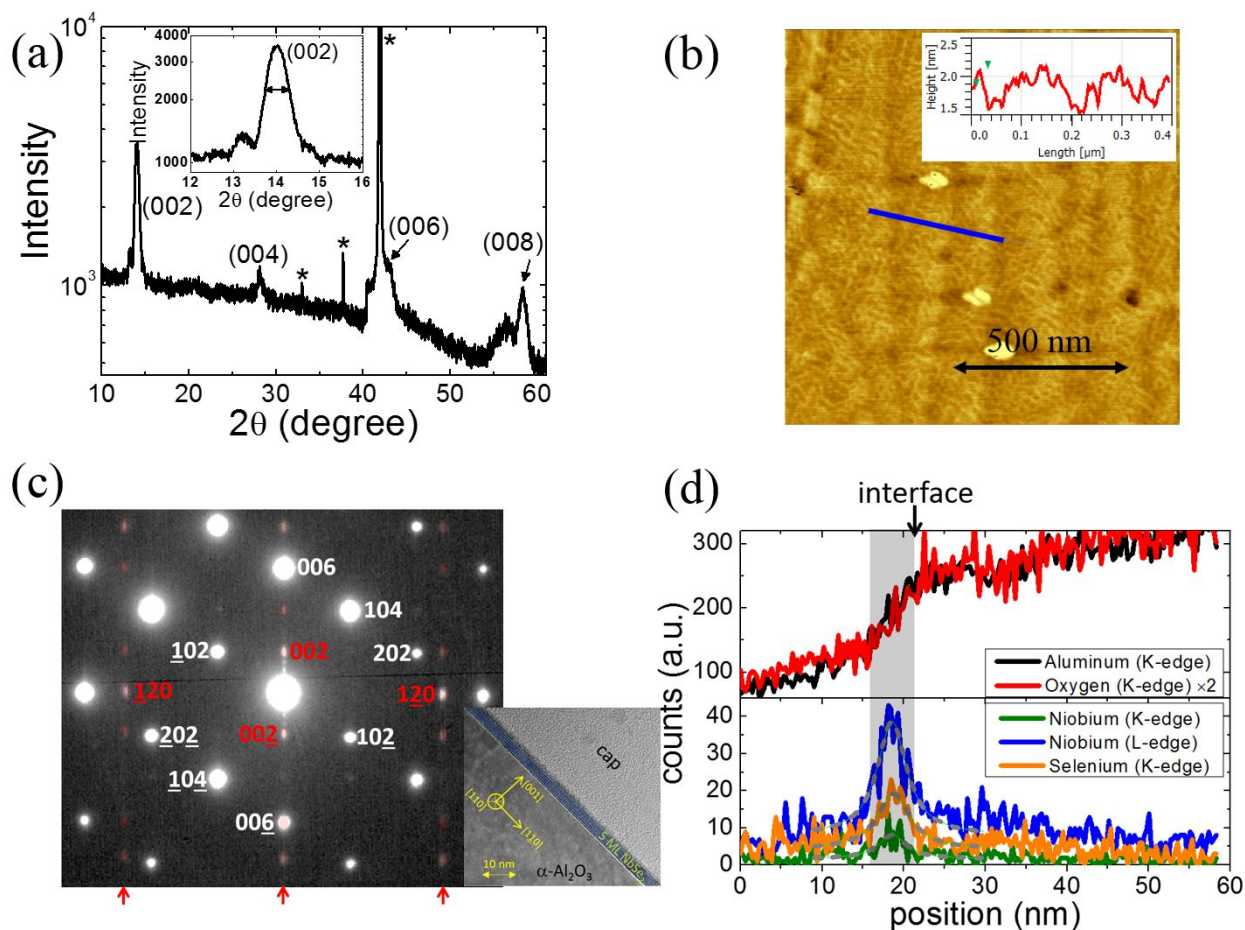


Fig. 2. (a) The X-ray diffraction of a NbSe₂ sample. The well oriented *c*-axis diffraction peaks are seen. The starred peaks correspond to the substrate and the background from the instrument. The inset provides a magnified image of the (002) peak, which also shows signatures of thickness fringes. (b) The AFM image of a continuous (islands-free) 3 ML NbSe₂ sample following the growth procedure shown in SI. The substrate terraces are visible indicating good surface coverage. (c) The TEM based selective area diffraction (SAD) data of the 5 ML NbSe₂ sample (inset). The substrate diffraction peaks are labeled in white and the NbSe₂ diffraction peaks are in red. The *c*-axis (002) diffraction of NbSe₂ is aligned with the *c*-axis (006) diffraction of sapphire. (d) The element selective spatially resolved energy dispersive X-ray spectroscopy (EDX) data of a line across the interface of the layer. The data shows no element segregations in the layer and a clear

1
2
3 interface with the substrate. The stoichiometric ratio between Nb and Se is determined in Fig S2b
4
5 in the SI.
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

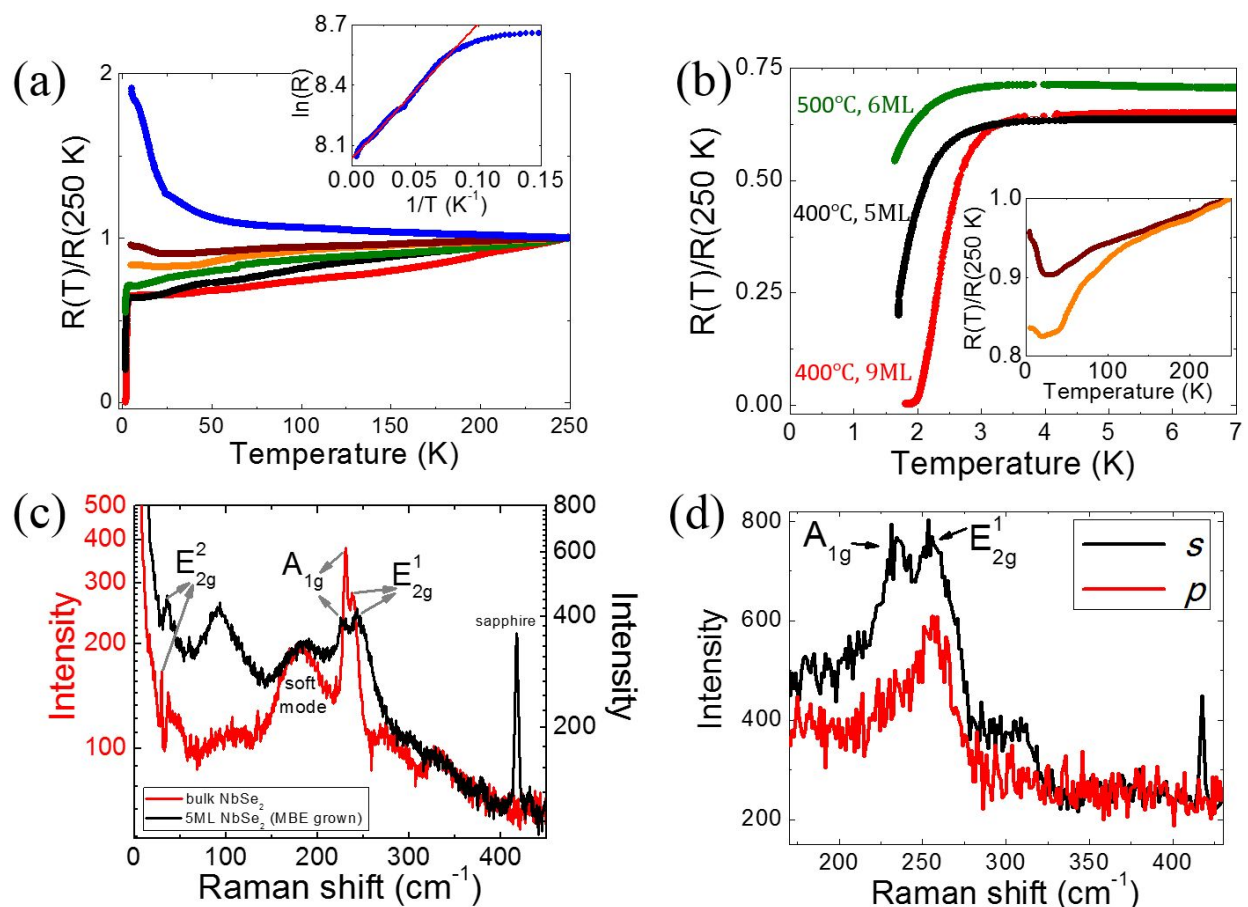
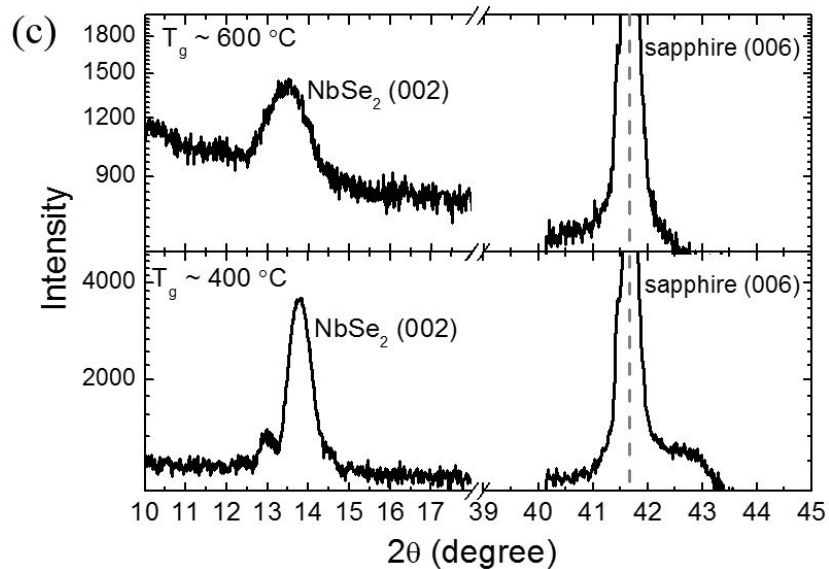
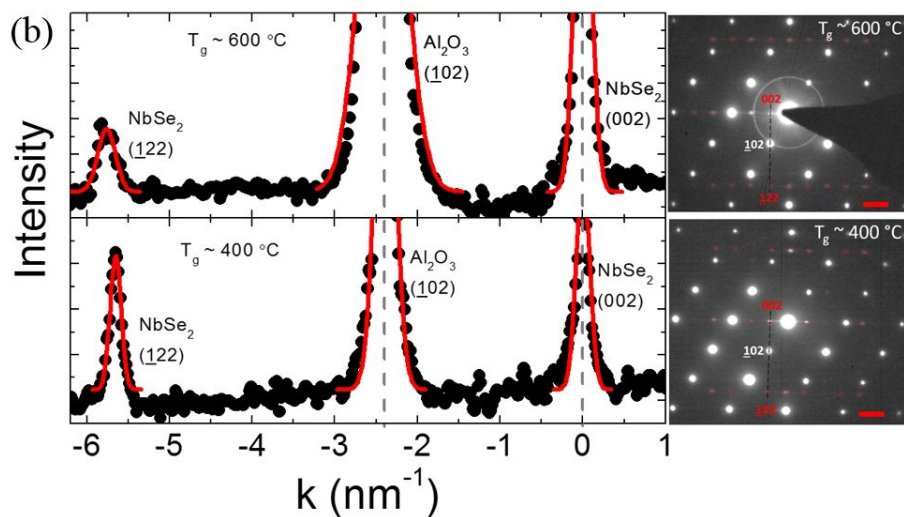
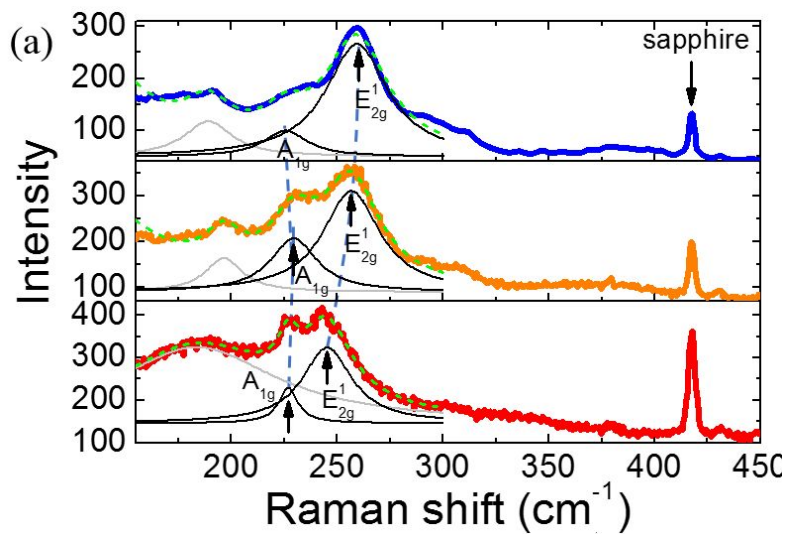
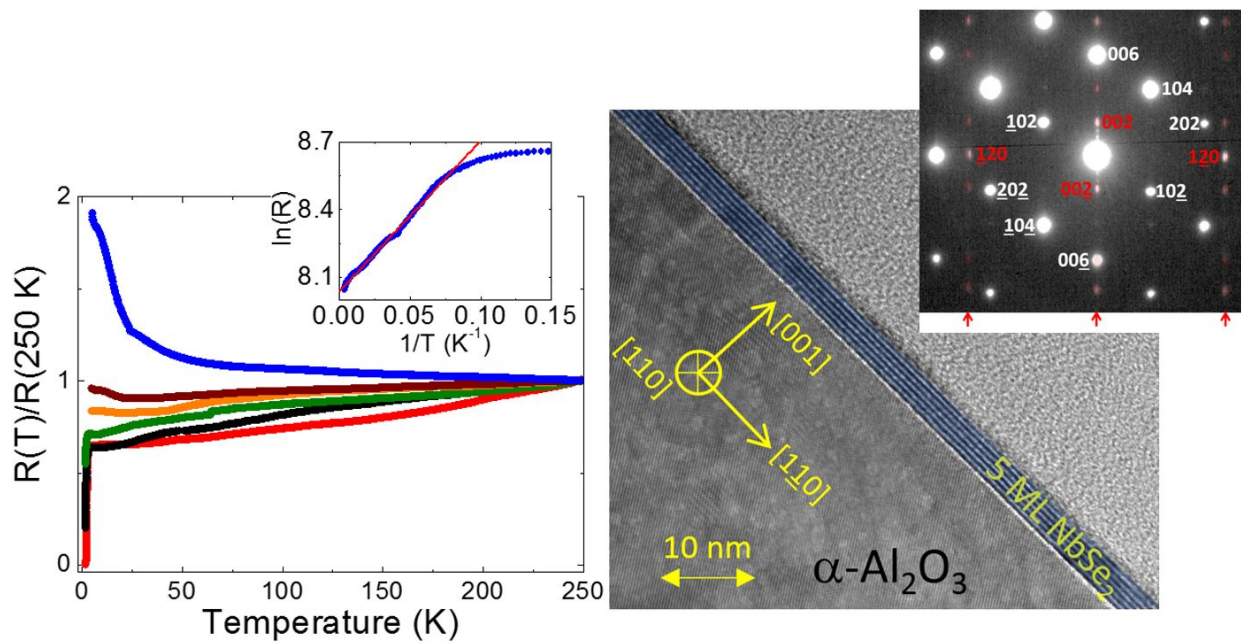


Fig. 3. (a) Resistance measurements of the superconductor to insulator transition in NbSe₂ samples systematically tuned by varying the growth temperature (from 400 °C to 600 °C). Inset: the $\ln(R)$ vs. $1/T$ plot of the insulating sample. The linear fit works in the full temperature range from 13 K and above, which gives an excitation gap $\frac{E_0}{k_B} \sim 6.7$ K. (b) The low temperature zoomed-in plot of the superconducting samples. Inset: the metallic samples demonstrating low temperature insulating behavior. The color of each curve matches that of (a). (c) Raman spectra comparison between MBE grown superconducting NbSe₂ (black) and a bulk sample (red). The MBE grown sample has a blue shift for E_{2g}^1 and a red shift for A_{1g} . (d) Polarized Raman spectroscopy confirming both the A_{1g} and E_{2g}^1 Raman modes of the sample shown in the middle panel of Fig 4a. The A_{1g} is turned off when switching from s - to p -polarization, whereas the E_{2g}^1 peak survives.



1
2
3 **Fig. 4.** (a) A comparison of the Raman spectra among three samples having different electrical
4 properties (the superconducting sample, the insulating sample and a sample in between). The color
5 of the data matches that in Fig. 3a. Two-peak Gaussian fit is used to identify the locations of the
6 E_{2g}^1 and A_{1g} peaks. A red shift of the A_{1g} peak and a blue shift of the E_{2g}^1 peak are observed, which
7 accompanies the loss of superconductivity. The comparison is guaranteed by the aligned sapphire
8 peak. (b) The comparison of the SAD results of two samples grown at $T_g \sim 600$ °C (top, insulating)
9 and at $T_g \sim 400$ °C (bottom, superconducting) respectively. A line cut is made from the $NbSe_2$
10 SAD (002) peak to the $NbSe_2$ SAD ($\bar{1}22$) peak crossing the sapphire SAD ($\bar{1}02$) peak. The line
11 cut is indicated by the dashed line shown in the TEM images (right). Gaussian fit is used to identify
12 the locations of the diffraction peak. By aligning the $NbSe_2$ (002) and sapphire ($\bar{1}02$) peaks (left),
13 one can see a clear shift of $NbSe_2$ ($\bar{1}22$) peak indicating that the sample grown at $T_g \sim 600$ °C has
14 a slightly smaller lattice constant. (c) The XRD results of two samples grown at $T_g \sim 600$ °C (top)
15 and at $T_g \sim 400$ °C (bottom). The $NbSe_2$ (002) XRD peak shifts to lower angle for the sample
16 grown at $T_g \sim 600$ °C suggesting an expanded c -axis lattice constant. The comparison is based on
17 the aligned sapphire (006) XRD peak.

Table of Contents (TOC) graphic



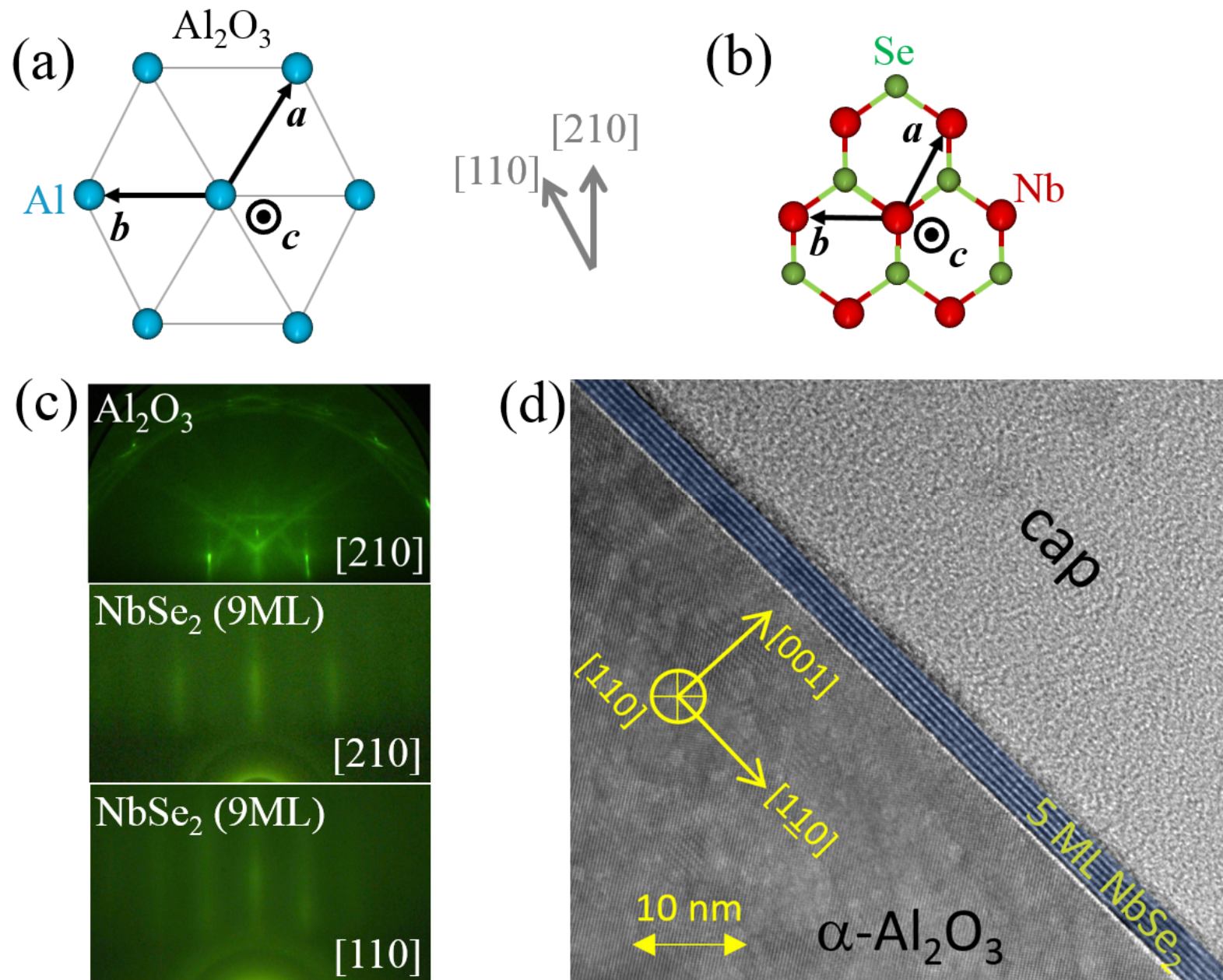
Supporting Information: including Sample growth (S1), Sample characterization (S2), Variable range hopping fitting to the insulating sample (S3), DFT calculations of the phonon spectrum of 1T-NbSe₂ (S4)

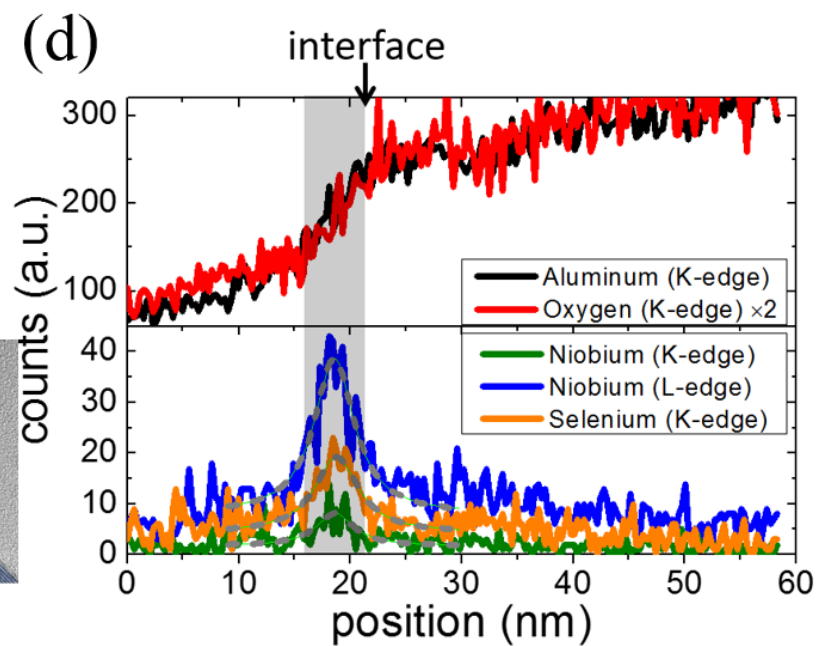
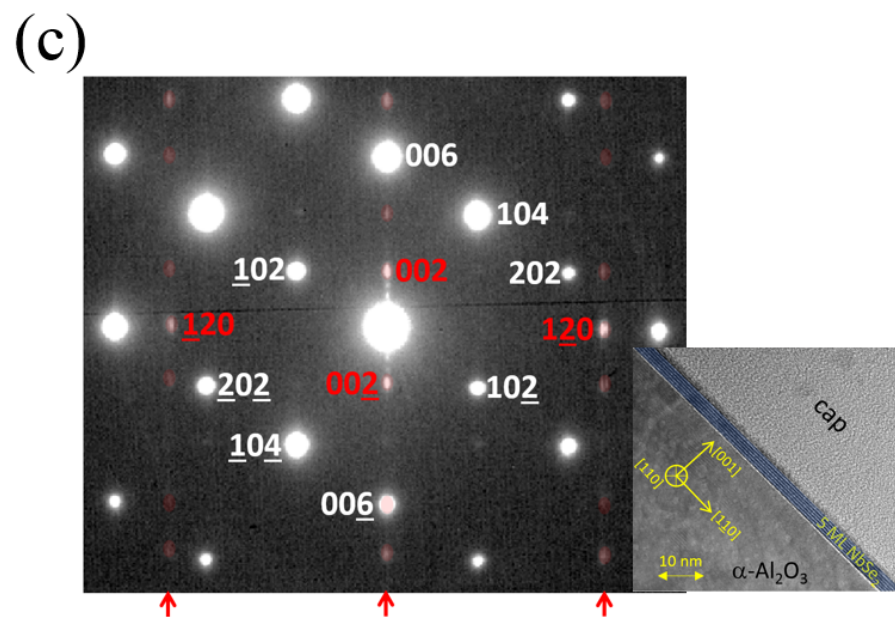
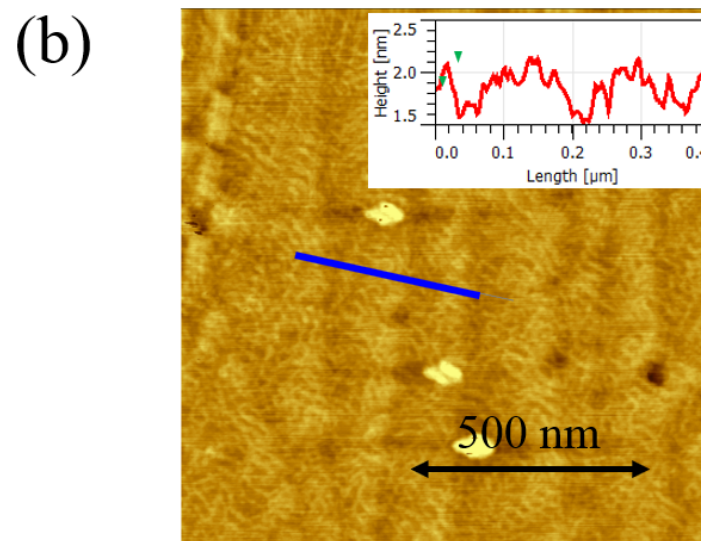
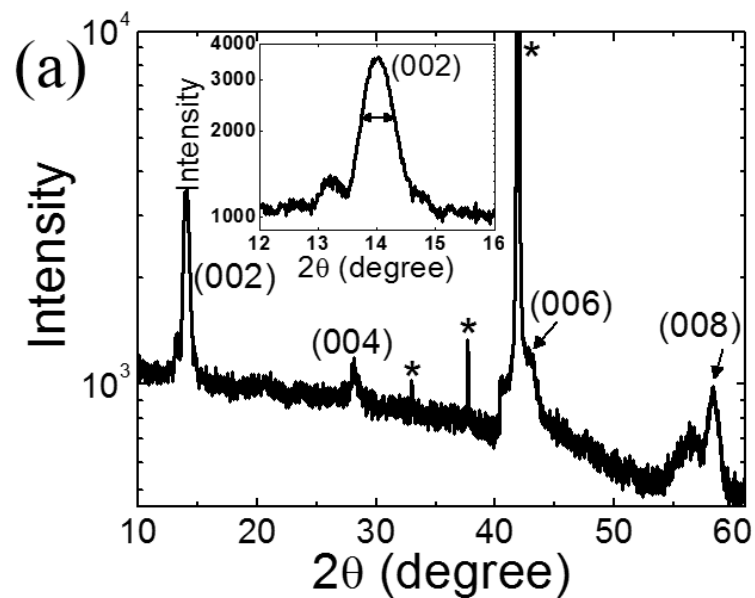
References:

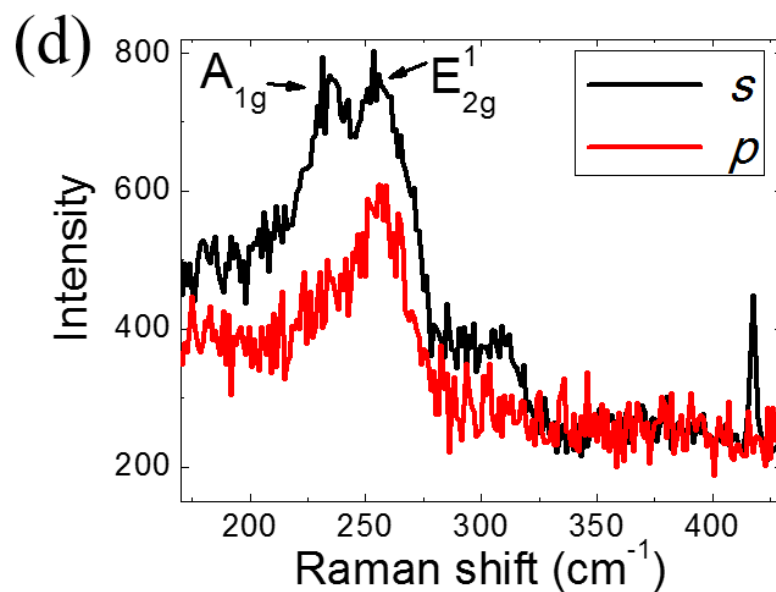
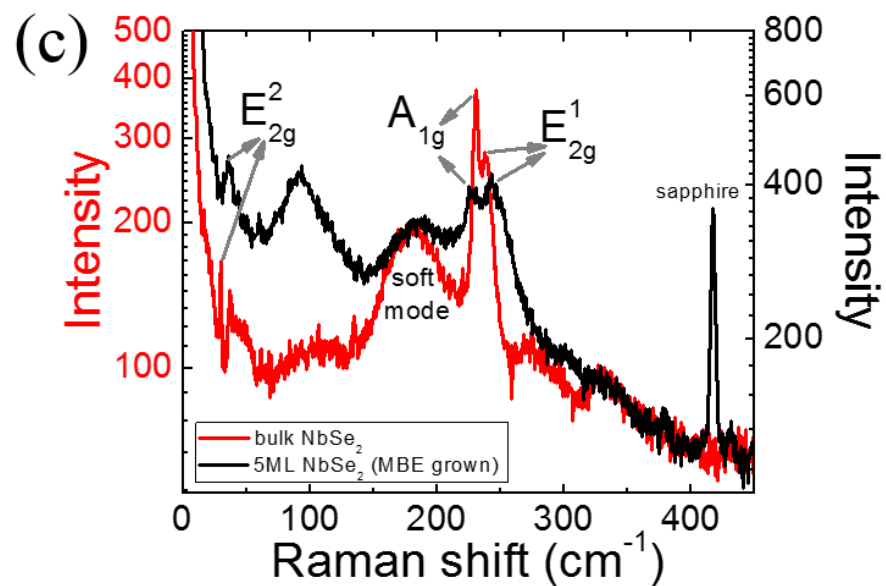
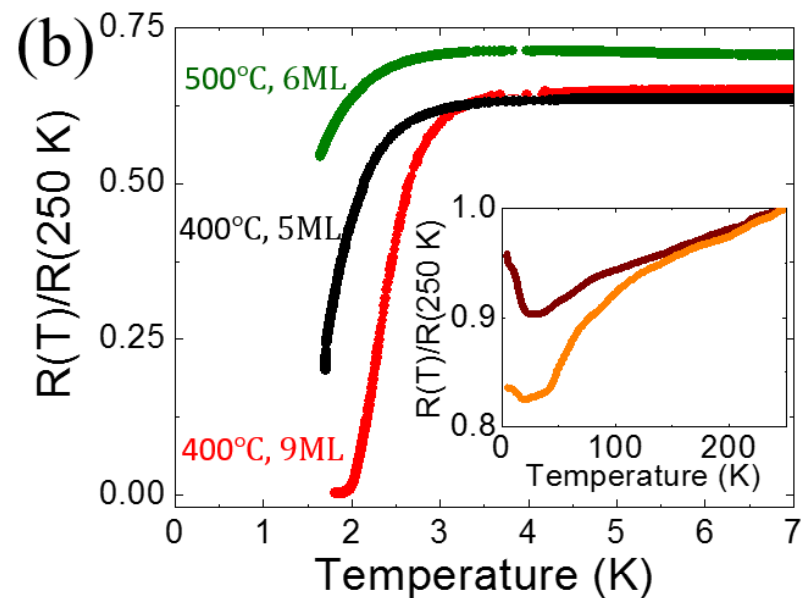
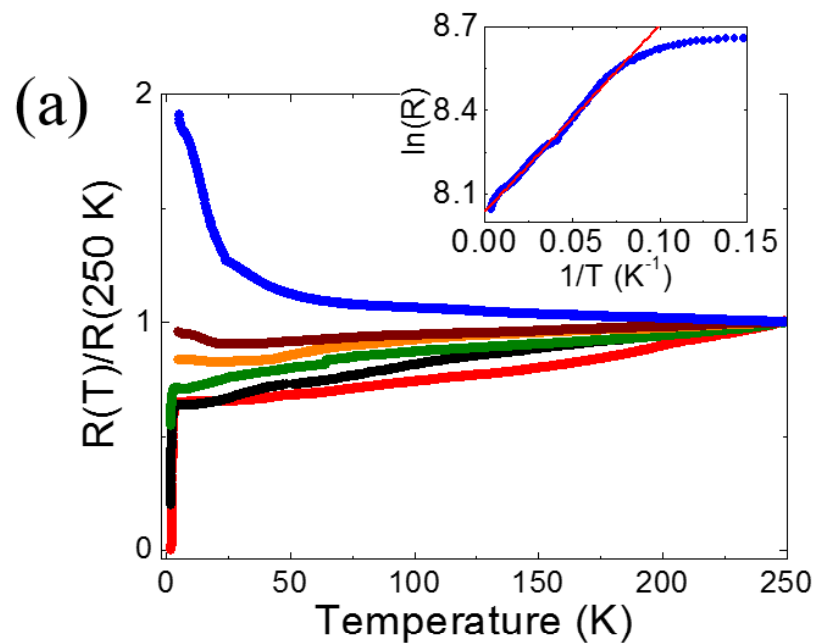
- 1 Kitaev, A. Y. Unpaired Majorana fermions in quantum wires. *Phys-Usp+* **44**, 131, (2001).
- 2 Xi, X., Wang, Z., Zhao, W., Park, J.-H., Law, K. T., Berger, H., Forro, L., Shan, J. & Mak, K. F. Ising pairing in superconducting NbSe₂ atomic layers. *Nat Phys* **12**, 139-143, (2016).
- 3 Xing, Y., Zhao, K., Shan, P., Zheng, F., Zhang, Y., Fu, H., Liu, Y., Tian, M., Xi, C., Liu, H., Feng, J., Lin, X., Ji, S., Chen, X., Xue, Q.-K. & Wang, J. Ising Superconductivity and Quantum Phase Transition in Macro-Size Monolayer NbSe₂. *Nano Lett* **17**, 6802-6807, (2017).
- 4 de la Barrera, S. C., Sinko, M. R., Gopalan, D. P., Sivadas, N., Seyler, K. L., Watanabe, K., Taniguchi, T., Tsen, A. W., Xu, X., Xiao, D. & Hunt, B. M. Tuning Ising superconductivity with layer and spin-orbit coupling in two-dimensional transition-metal dichalcogenides. *Nat Commun* **9**, 1427, (2018).
- 5 Zhou, B. T., Yuan, N. F. Q., Jiang, H.-L. & Law, K. T. Ising superconductivity and Majorana fermions in transition-metal dichalcogenides. *Phys Rev B* **93**, 180501, (2016).
- 6 Triola, C., Badiane, D. M., Balatsky, A. V. & Rossi, E. General Conditions for Proximity-Induced Odd-Frequency Superconductivity in Two-Dimensional Electronic Systems. *Phys Rev Lett* **116**, 257001, (2016).
- 7 Hsu, Y.-T., Vaezi, A., Fischer, M. H. & Kim, E.-A. Topological superconductivity in monolayer transition metal dichalcogenides. *Nat Commun* **8**, 14985, (2017).
- 8 Rahimi, M. A., Moghaddam, A. G., Dykstra, C., Governale, M. & Zülicke, U. Unconventional superconductivity from magnetism in transition-metal dichalcogenides. *Phys Rev B* **95**, 104515, (2017).
- 9 He, W.-Y., Zhou, B. T., He, J. J., Yuan, N. F. Q., Zhang, T. & Law, K. T. Magnetic field driven nodal topological superconductivity in monolayer transition metal dichalcogenides. *Communications Physics* **1**, 40, (2018).
- 10 Xi, X., Zhao, L., Wang, Z., Berger, H., Forró, L., Shan, J. & Mak, K. F. Strongly enhanced charge-density-wave order in monolayer NbSe₂. *Nat Nanotechnol* **10**, 765, (2015).
- 11 Bischoff, F., Auwärter, W., Barth, J. V., Schiffrin, A., Fuhrer, M. & Weber, B. Nanoscale Phase Engineering of Niobium Diselenide. *Chem Mater* **29**, 9907-9914, (2017).
- 12 Nakata, Y., Sugawara, K., Shimizu, R., Okada, Y., Han, P., Hitosugi, T., Ueno, K., Sato, T. & Takahashi, T. Monolayer 1T-NbSe₂ as a Mott insulator. *NPG Asia Mater* **8**, e321, (2016).
- 13 Ugeda, M. M., Bradley, A. J., Zhang, Y., Onishi, S., Chen, Y., Ruan, W., Ojeda-Aristizabal, C., Ryu, H., Edmonds, M. T., Tsai, H.-Z., Riss, A., Mo, S.-K., Lee, D., Zettl, A., Hussain, Z., Shen, Z.-X. & Crommie, M. F. Characterization of collective ground states in single-layer NbSe₂. *Nat Phys* **12**, 92, (2015).
- 14 Mattheiss, L. F. Band Structures of Transition-Metal-Dichalcogenide Layer Compounds. *Phys Rev B* **8**, 3719-3740, (1973).
- 15 Nakano, M., Wang, Y., Kashiwabara, Y., Matsuoka, H. & Iwasa, Y. Layer-by-Layer Epitaxial Growth of Scalable WSe₂ on Sapphire by Molecular Beam Epitaxy. *Nano Lett* **17**, 5595-5599, (2017).

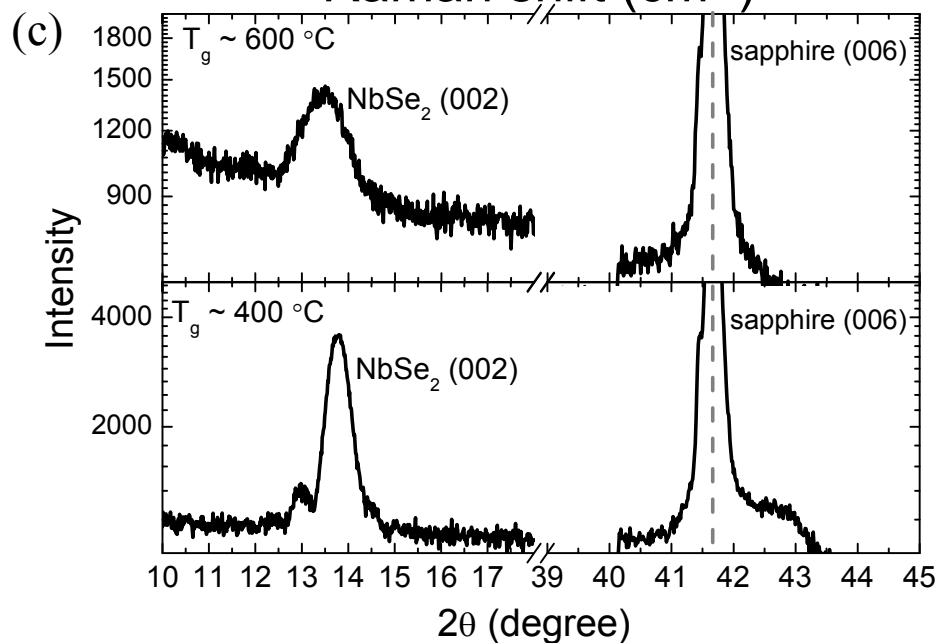
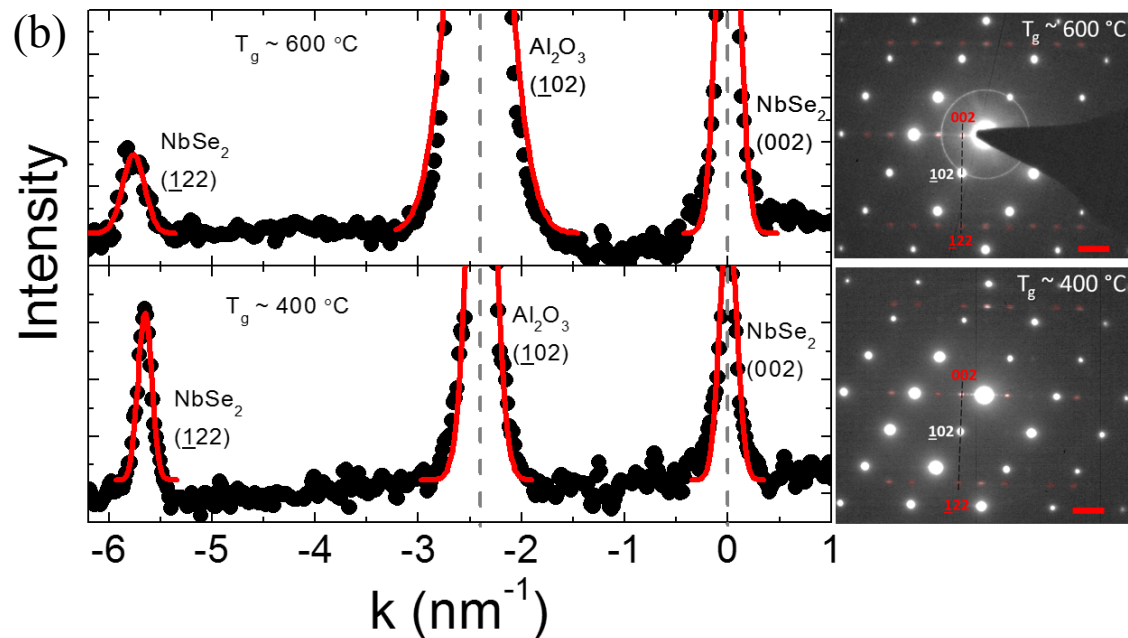
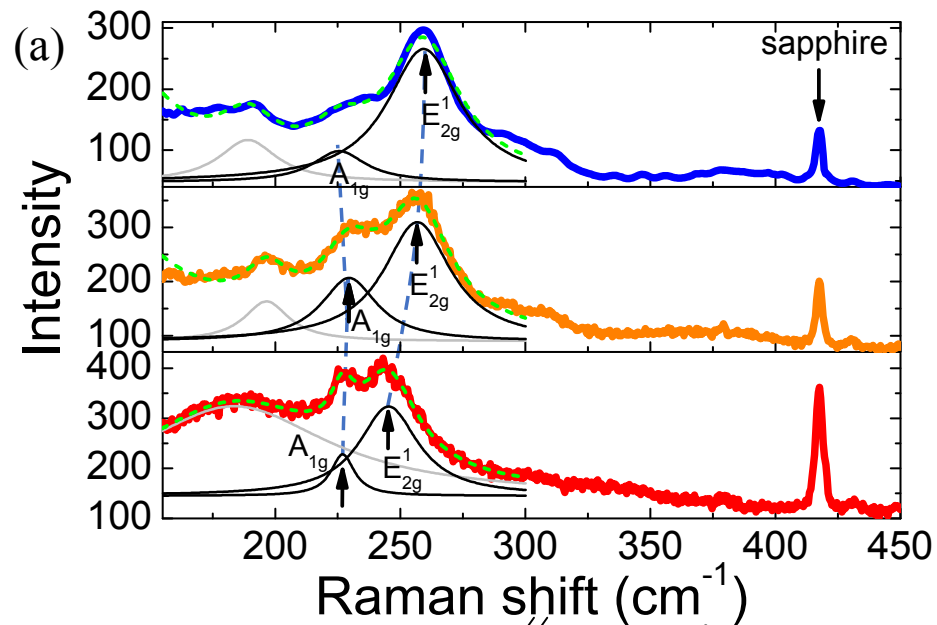
- 1
2
3 16 Moser, J., Matos-Abiague, A., Schuh, D., Wegscheider, W., Fabian, J. & Weiss, D.
4 Tunneling Anisotropic Magnetoresistance and Spin-Orbit Coupling in Fe/GaAs/Au
5 Tunnel Junctions. *Phys Rev Lett* **99**, 056601, (2007).
6
7 17 Žutić, I., Matos-Abiague, A., Scharf, B., Dery, H. & Belashchenko, K. Proximitized
8 materials. *Mater Today* **22**, 85-107, (2019).
9
10 18 Samnakay, R., Wickramaratne, D., Pope, T. R., Lake, R. K., Salguero, T. T. & Balandin,
11 A. A. Zone-Folded Phonons and the Commensurate–Incommensurate Charge-Density-
12 Wave Transition in 1T-TaSe₂ Thin Films. *Nano Lett* **15**, 2965-2973, (2015).
13
14 19 Aytan, E., Debnath, B., Kargar, F., Barlas, Y., Lacerda, M. M., Li, J. X., Lake, R. K., Shi,
15 J. & Balandin, A. A. Spin-phonon coupling in antiferromagnetic nickel oxide. *Appl Phys*
16 *Lett* **111**, 252402, (2017).
17
18 20 Pak, S., Lee, J., Lee, Y.-W., Jang, A. R., Ahn, S., Ma, K. Y., Cho, Y., Hong, J., Lee, S.,
19 Jeong, H. Y., Im, H., Shin, H. S., Morris, S. M., Cha, S., Sohn, J. I. & Kim, J. M. Strain-
20 Mediated Interlayer Coupling Effects on the Excitonic Behaviors in an Epitaxially Grown
21 MoS₂/WS₂ van der Waals Heterobilayer. *Nano Lett* **17**, 5634-5640, (2017).
22
23 21 Pereira, C. M. & Liang, W. Y. Raman studies of the normal phase of 2H-NbSe₂. *Journal*
24 *of Physics C: Solid State Physics* **15**, L991, (1982).
25
26 22 Bardeen, J., Cooper, L. N. & Schrieffer, J. R. Theory of Superconductivity. *Phys Rev*
27 **108**, 1175-1204, (1957).
28
29 23 Fu, Y., Liu, E., Yuan, H., Tang, P., Lian, B., Xu, G., Zeng, J., Chen, Z., Wang, Y., Zhou,
30 W., Xu, K., Gao, A., Pan, C., Wang, M., Wang, B., Zhang, S.-C., Cui, Y., Hwang, H. Y.
31 & Miao, F. Gated tuned superconductivity and phonon softening in monolayer and
32 bilayer MoS₂. *npj Quantum Materials* **2**, 52, (2017).
33
34 24 Hui, Y. Y., Liu, X., Jie, W., Chan, N. Y., Hao, J., Hsu, Y.-T., Li, L.-J., Guo, W. & Lau,
35 S. P. Exceptional Tunability of Band Energy in a Compressively Strained Trilayer MoS₂
36 Sheet. *Acs Nano* **7**, 7126-7131, (2013).
37
38 25 Staley, N. E., Wu, J., Eklund, P., Liu, Y., Li, L. & Xu, Z. Electric field effect on
39 superconductivity in atomically thin flakes of NbSe₂. *Phys Rev B* **80**, 184505, (2009).
40
41 26 El-Bana, M. S., Wolverson, D., Russo, S., Balakrishnan, G., Paul, D. M. & Bending, S. J.
42 Superconductivity in two-dimensional NbSe₂ field effect transistors. *Superconductor*
43 *Science and Technology* **26**, 125020, (2013).
44
45 27 Xi, X., Berger, H., Forró, L., Shan, J. & Mak, K. F. Gate Tuning of Electronic Phase
46 Transitions in Two-Dimensional NbSe₂. *Phys Rev Lett* **117**, 106801, (2016).
47
48 28 Ye, J. T., Zhang, Y. J., Akashi, R., Bahramy, M. S., Arita, R. & Iwasa, Y.
49 Superconducting Dome in a Gate-Tuned Band Insulator. *Science* **338**, 1193, (2012).
50
51 29 Zhou, T., Dartailh, M. C., Mayer, W., Han, J. E., Matos-Abiague, A., Shabani, J. &
52 Žutić, I. Phase Control of Majorana Bound States in a Topological X Junction. *Phys Rev*
53 *Lett* **124**, 137001, (2020).
54
55 30 Wang, Z., Tang, C., Sachs, R., Barlas, Y. & Shi, J. Proximity-Induced Ferromagnetism in
56 Graphene Revealed by the Anomalous Hall Effect. *Phys Rev Lett* **114**, 016603, (2015).
57
58 31 Wei, P., Lee, S., Lemaitre, F., Pinel, L., Cutaia, D., Cha, W., Katmis, F., Zhu, Y.,
59 Heiman, D., Hone, J., Moodera, J. S. & Chen, C.-T. Strong interfacial exchange field in
60 the graphene/EuS heterostructure. *Nat Mater* **15**, 711, (2016).
32 Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized Gradient Approximation Made
Simple. *Phys Rev Lett* **77**, 3865-3868, (1996).

- 1
2
3 33 Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-
4 wave method. *Phys Rev B* **59**, 1758-1775, (1999).
5 34 Grimme, S. Semiempirical GGA-type density functional constructed with a long-range
6 dispersion correction. *J Comput Chem* **27**, 1787-1799, (2006).
7 35 Towns, J., Cockerill, T., Dahan, M., Foster, I., Gaither, K., Grimshaw, A., Hazlewood,
8 V., Lathrop, S., Lifka, D., Peterson, G. D., Roskies, R., Scott, J. R. & Wilkins-Diehr, N.
9 XSEDE: Accelerating Scientific Discovery. *Comput Sci Eng* **16**, 62-74, (2014).
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60









1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46