Superconductor to insulator transition in wafer-scale NbSe$_2$

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Abstract: Superconducting tunneling devices, such as Josephson junctions etc., that are made of triplet or topological superconductors may enable new functionalities compared to those conventional ones made of $s$-wave superconductors. The tunnel barrier, an insulating or normal material layer separating two superconductors, is an important component for the Josephson tunneling devices. Thin layers of NbSe$_2$ have been shown to manifest Ising superconductivity behavior, which can give rise to topological superconductivity driven by large magnetic exchange field. Here we demonstrate the control between superconducting and insulating phases of NbSe$_2$ in epitaxially grown samples with wafer-scale uniformity. We provide the first electrical transport and Raman spectroscopy characterizations of the insulating phase, and show that the energy shift of the Raman modes is closely tied to the phase transition. Our observation paves the way for high quality heterojunction tunnel barriers to be seamlessly built into NbSe$_2$ itself, thereby enabling highly scalable tunneling devices for superconductor-based quantum electronics.

Keywords: two-dimensional layered superconductor, epitaxial heterostructure
The structural phase transition of NbSe$_2$ is a potential knob for controlling superconductivity. NbSe$_2$ is often found in its prismatic 2H phase, i.e. the superconducting phase, in devices fabricated from exfoliated thin crystals.\textsuperscript{2,4,10} Insulating NbSe$_2$ is rare\textsuperscript{11} although it has been recently demonstrated that the epitaxially grown 1T phase NbSe$_2$ is an insulator who features a gapped Fermi surface as confirmed by angled resolved photo emission (ARPES).\textsuperscript{12} Up to now, there has yet been a demonstration of the controlled phase transition from superconducting to insulating in NbSe$_2$. Besides, the epitaxial growth of superconducting NbSe$_2$ has been limited to graphene substrates.\textsuperscript{3,13} Compared to insulating substrates, such as sapphire, the high conductivity of graphene substrate do not favor the fabrication of planar Josephson tunneling devices, which are critical for the scalable circuity of topological superconductors.\textsuperscript{14,15}

We have successfully achieved wafer-scale few-layer NbSe$_2$ grown on sapphire substrates using MBE. Because the substrate is highly insulating, we are able to carry out the first electrical transport characterizations of both phases. We confirm an insulating or semiconducting phase of NbSe$_2$, which features a fully gapped Fermi surface. Previously, the Raman spectrum has been limited to 2H-NbSe$_2$. We now show the Raman spectrum of insulating NbSe$_2$, and we find that the two crystallographic phases are closely related but clearly distinguished by the shift of their characteristic Raman peaks, which indicates the hardening or softening of the lattice vibration modes. It thus provides insight to the transition between the insulating and superconducting electronic properties of the two phases.

The quality of our epitaxially grown NbSe$_2$, including crystal symmetry and epitaxial orientation, is confirmed by in-situ refractive high energy electron diffraction (RHEED) (Fig. 1a and 1b). A 0.5 monolayer (ML) NbSe$_2$ seed, which does not completely cover the sapphire substrate (Fig. 1c and 1d), is used to facilitate the growth (see SI). The hexagonal symmetry of the
grown layer is confirmed by a planar rotation of the RHEED electron beam from [210] (Fig. 1e) to [110] (Fig. 1f) directions. Using the diffraction data, we calculate the lattice constant to be ~3.42 Å (error within 12%), matching closely to that of NbSe2. The NbSe2 layer does not match with the substrate and has a much smaller lattice constant compared to that of the c-cut sapphire (lattice constant ~ 4.76 Å), which is also seen by the dramatic increase of the RHEED streak spacing (Fig. 1c and 1e). However, the two lattices match better with each other by considering the 3×3 unit cells of NbSe2 and the 2×2 unit cells of sapphire, which gives only ~7.8% mismatch and could instead impose a compressive strain effect in NbSe2. Such matching of the superlattice cells has been previously reported regarding the growth of high quality transition-metal dichalcogenides (TMD) on sapphire substrate. Besides, it is clear that the crystalline orientations of NbSe2 and sapphire are locked as [210]NbSe2 // [210]sapphire (Fig. 1c and Fig. 1e), which may lead to strain effect and infers that there is an interaction between NbSe2 and the substrate.

The wafer-scale coverage and grain size of NbSe2 are confirmed by both x-ray diffraction (XRD) and atomic force microscopy (AFM) (Fig. 2a and 2b). XRD proves the quality of NbSe2 by demonstrating a set of clear diffraction peaks (Fig. 2a). The estimated c-axis lattice constant ~12.61 Å matches well with those reported for bulk NbSe2 samples. Interestingly, each grain does not form an isolated island even in thin samples. For NbSe2 as thin as 3 ML, AFM shows that the grown NbSe2 layer develops terrace-like features (Fig. 2b), which originate from the terraces of sapphire and indicate good NbSe2 coverage without islands.

A systematic tuning of superconductivity in NbSe2 is achieved by controlling the growth condition (Fig. 3a). Both increasing the growth temperature and decreasing the layer thickness cause a decrease of $T_c$ (Fig. 3b). As the growth temperature further increases, the sample starts to develop a sharp resistance upturn at low temperature (Fig. 3b inset). To clarify the origin of the
resistance upturn, we increase the growth temperature to 600 °C, which gives rise to an insulating NbSe₂ sample in the full temperature range (Fig. 3a blue). A plot of ln(R) vs. T⁻¹ is used to validate the origin of the insulating behavior (Fig. 3c). We find that a linear fit well describes the ln(R) vs. T⁻¹ plot (Fig. 3c) in a wide temperature range (13 K and above), which is not the case if a variable-range hopping model is used (see SI). Thus, such insulating behavior is not due to localization effects caused by defects. It confirms a fully gapped Fermi surface with the conductivity given by \( \sigma \sim e^{-\frac{E_g}{k_BT}} \), where the activation energy determined to be \( \frac{E_g}{k_B} \sim 6.7 \) K.

Interestingly, we find that both the insulating and superconducting NbSe₂ have the same lattice constants (Fig. 3d) (no differences within the resolution of RHEED), and the same hexagonal rotation symmetry (Fig. 3d). The insulating sample has even sharper and better defined RHEED streaks indicating better crystal quality, which is consistent with the high growth temperature.

Although electron and X-ray diffraction could not tell the structural difference between the superconducting and insulating NbSe₂, it is visible in Raman spectroscopy, which is known to be sensitive to various phase transitions in a wide range of materials. The Raman spectrum of a 5 ML superconducting sample is compared to that of a bulk NbSe₂ sample in Fig. 4a. The two spectra resemble each other by both showing the A₁g, E₁₂g and the soft mode peaks with comparable intensities, which proves the quality of the MBE grown layer. Compared to bulk NbSe₂, it is clear that the E₁₂g peak of the MBE grown NbSe₂ blue shifts to a higher wave number, while the A₁g peak red shifts to a lower wave number (Fig. 4a). Such shift is also visible for the E²₂g peak. The nature of the E₁₂g and A₁g vibration modes is further confirmed by polarized Raman spectroscopy (Fig. 4b), in which the p-polarization turns off the A₁g peak while maintaining the E₁₂g peak, consistent with prior reports in 2H-NbSe₂. The blue shift of E₁₂g or the red shift of A₁g is related to the hardening or softening of phonons, which is often a result of the change of lattice
parameters caused by strain. The $E_{12g}$ mode describes the planar lattice vibrations of NbSe$_2$ (Fig. 4c). Its blue shift thus suggests a decrease of the $a$ lattice constant due to a planar compressive strain, which is possible by considering the 7.8% smaller sapphire supercell compared to that of NbSe$_2$. On the other hand, the reduction of the $a$ lattice constant results in an increase of the $c$ lattice constant causing a red shift to the $A_{1g}$ mode that describes the out-of-plane lattice vibrations (Fig. 4c). The hardening of the phonon mode that corresponds to $E_{12g}$ could affect the superconductivity of NbSe$_2$.

To further find out the effect on superconductivity due to the change of phonon mode, we carried out a series of Raman spectroscopy experiments focusing on the shift of the $E_{12g}$ and $A_{1g}$ peaks (Fig. 4d). The measurement is done in a set of NbSe$_2$ samples ranging from superconducting to insulating. The resistance as a function of temperature is plotted in Fig. 3a. A dramatic increase of the $E_{12g}$ peak, from 245 cm$^{-1}$ to 260 cm$^{-1}$ is observed as NbSe$_2$ loses superconductivity and becomes insulating (Fig. 4d). The validity of the comparison is guaranteed by the aligned sapphire substrate Raman peak at 418 cm$^{-1}$. According to BCS theory, the electron-phonon coupling strength is weakened when the stiffness of the lattice vibrations increases, which has been observed in other 2D materials such as MoS$_2$. The switching-off of superconductivity in our metallic NbSe$_2$ (Fig. 3a and 3b) could be a consequence of phonon hardening. Also, compared to bulk NbSe$_2$ (Fig. 4a), the slight blue shift of $E_{12g}$ could further explain the lowered $T_c$ in the MBE grown 5 ML NbSe$_2$.

Although the lattice constant and the hexagonal symmetry are the same for both the superconducting and insulating NbSe$_2$ samples (Fig. 3d), a $E_{12g}$ peak as large as 260 cm$^{-1}$ was not previously observed in 2H-NbSe$_2$. Such a $E_{12g}$ peak that is located at higher wave number could be a result of strain due to the substrate. For NbSe$_2$ grown on sapphire, the strain effect is stronger
as the crystallinity of the grown layer is better. This is the case for insulating NbSe$_2$ grown at a higher temperature as seen by the sharper RHEED streaks in Fig. 3d. Therefore, we expect a stronger blue shift of $E^{12g}$ in insulating NbSe$_2$. For TMD material, a compressive strain often leads to an increase of the band gap,$^{24}$ which may account for the insulating behavior in our NbSe$_2$ grown at high temperatures. Besides, it has been reported that 1T-NbSe$_2$ is a Mott insulator, which is obtained by growing NbSe$_2$ at a higher substrate temperature.$^{12}$ Our density functional theory (DFT) calculations show that the Raman activated modes are very different between 2H-NbSe$_2$ and 1T-NbSe$_2$ (see SI). Therefore, our observation that shows a continuous blue shift of the $E^{12g}$ peak (Fig. 4d) is likely not due to the 2H to 1T transition in NbSe$_2$.

Nevertheless, our results on the superconducting to insulating transition in NbSe$_2$ shows that few-layer NbSe$_2$ can also behave as a fully gapped semiconductor demonstrating insulating behavior (Fig. 3c) and a controlled tuning of such transition is achievable. The insulating phase in NbSe$_2$ could serve as a high-quality tunnel barrier material with a good lattice match with the superconducting 2H-NbSe$_2$, thereby would enable a range of superconducting tunneling devices to be seamlessly built into NbSe$_2$. Combining with other materials that generate large magnetic exchange fields in layered 2D materials,$^{25,26}$ the heterostructures of NbSe$_2$ are promising candidates for topological superconductors. The wafer-scale NbSe$_2$ with controlled crystallographic phase can provide a platform for scalable superconducting electronics built on triplet superconductors.

**Methods:**

Growth of the NbSe$_2$ 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 100μm 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 in a liquid helium dewar. Temperature was controlled by adjusting the insertion height of the probe. The temperatures below 4.2K were achieved by letting additional He gas condense inside the probe followed by pumping to reduce the vapor pressure. A Stanford Research Systems lock-in amplifier was used to measure the resistance of the films in a four-terminal configuration. The DFT calculations were carried out within the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation and the projected augmented wave (PAW) method as implemented in software package VASP.27,28

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Figures and captions:

![Diagram of Al atoms on sapphire (0001) surface](image1)

![Diagram of NbSe2 surface and its epitaxial orientation](image2)

(c) \[\text{Al}_2\text{O}_3\]

(d) seed (0.5 ML)

(e) \[\text{NbSe}_2\ (9\text{ML})\]

(f) \[\text{NbSe}_2\ (9\text{ML})\]

**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). There is a significant ~39% shrinking of the lattice constant comparing NbSe2 with sapphire. (c) The RHEED pattern of sapphire substrate along [210] direction. (d) The RHEED of 0.5 ML NbSe2 seed layer after annealing. (e) and (f) The RHEED pattern of 9 ML NbSe2 along both [210] and [110] directions. The six-fold rotation symmetry and the extracted lattice constant both prove NbSe2.
**Fig. 2.** (a) The X-ray diffraction of a 20 nm NbSe$_2$ 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. The FWHM of the (002) peak is used to estimate the size of the crystallite (see SI). (b) The AFM image of a continuous (islands-free) 3 ML NbSe$_2$ sample grown at high temperature following the growth procedure shown in SI. The substrate terraces are visible indicating good surface coverage.
**Fig. 3.** (a) Resistance measurements of the superconductor to insulator transition in NbSe$_2$ samples systematically tuned by varying the growth temperature (from 400 °C to 600 °C). (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) 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. (d) The RHEED diffraction images comparing the crystal structures of insulating and superconducting NbSe$_2$. They both have similar six-fold planar rotation symmetry and comparable lattice constants. The RHEED image is sharper for the insulating sample, which is consistent to its high temperature growth.
Fig. 4. (a) Raman spectrum comparison between MBE grown superconducting NbSe$_2$ (black) with a bulk sample (red). The MBE grown sample has a blue shift for both the E$_{12g}$ and E$_{22g}$ peaks. (b) Polarized Raman spectroscopy confirming both the A$_{1g}$ and E$_{12g}$ Raman modes of the sample shown in the middle panel of (d). The A$_{1g}$ is turned off when switching from s- to p-polarization, whereas the E$_{12g}$ peak survives. (c) The schematic of the lattice vibrations corresponding to both the E$_{12g}$ and A$_{1g}$ modes. The E$_{12g}$ describes planar lattice vibration, while the A$_{1g}$ describes the out-of-plane vibration. (d) A comparison of the Raman spectra among three typical samples showing in Fig. 3a (the superconducting sample, the insulating sample and a sample in between). The color matches with that in Fig. 3a. A blue shift of the E$_{12g}$ peak is observed, which accompanies the loss of superconductivity. The A$_{1g}$ peak position is relatively constant. The comparison is guaranteed by the aligned sapphire peak.
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Supplementary Information:

Superconductor to insulator transition in wafer-scale NbSe₂

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S1. Growth and characterizations of thin layer NbSe₂:

Figure S1: (a) The atomic force microscopy (AFM) image of the sapphire (0001) substrate we used for growing wafer-scale NbSe₂. The inset show the height of the atomic terraces. (b) Outline of NbSe₂ thin film growth. Red and blue curves are for high temperature and low temperature growths respectively. Color shaded areas indicate intervals when the Nb shutter is open; Se shutter is kept open throughout entire growth. Beam interruption of the Nb flux is used in the low temperature main growth. (c) The grain structure of the layer is studied by FFT of the AFM image (inset). Six-fold symmetry of the FFT indicates the six-fold packing of the grains. Such six-fold closely packed grain is a result of the hexagonal shape of each grain.
The atomic terrace of the sapphire substrate (Fig. S1a) is obtained by annealing the substrate at 1200 °C in ambient environment for 5 hours. Prior to deposition, the sapphire substrates were degassed in-situ at 600°C for 30 minutes to remove surface adsorbents before cooling to the appropriate starting growth temperatures. The Nb and Se sources were heated via an electron beam evaporator and Knudsen cell, respectively. Fig. S1b outlines two of the growth procedures employed, one at low temperatures and one at high temperatures. For the low temperature growth, an amorphous buffer layer of Nb and Se is first deposited onto the substrate at room temperature in a similar manner as described in Ref [1] with a thickness of about half a monolayer. The buffer is subsequently annealed to 200°C at which point the main growth begins. We employ a beam interrupted method during the main growth in which the Nb shutter is cyclically closed and opened (10s open, 30s closed) to prevent excess Nb in the film as well as promote selenization of the Nb atoms. Meanwhile, the substrate heating is steadily raised to its final temperature of 400°C. After growth, the substrate is cooled to room temperature when it is capped with 30nm of Se. It should be noted that the Se flux is supplied continuously throughout the entire growth.

As for the high temperature growth procedure, we did not deposit a buffer layer nor did we employ any beam interruption of the Nb flux. Instead, the Nb and Se sources are co-evaporated onto the substrate continuously until the end of the growth at which point the substrate is cooled to room temperature and capped with 30nm of Se.

The morphology of the grown NbSe₂ layer is further studied in the reciprocal space by doing FFT to the real-space AFM image (main text Fig. 2b). A hexagonal pattern is observed (Fig. S1c). The hexagonal pattern in the FFT reciprocal space indicates that similar symmetry exists in the real space AFM image, which describes the hexagonal arrangement of the NbSe₂ grains. Such
hexagonal arrangement indicates that the grains are closely in touch with each other, i.e. no gaps in between, and the grains are hexagonally packed. This is a result of the hexagonal symmetry of the NbSe₂ crystal. Such observation is also consistent to the six-fold rotation symmetry observed by RHEED (main text Fig. 1), which proves that the grains are not randomly arranged.

**S2. Estimation of the crystallite size using XRD:**

The broadening of the (002) XRD peak (main text Fig. 2a) indicates finite crystallite size. The broadening $B$, defined as the FWHM of a specific diffraction peak, is described by Scherrer equation as $B = \frac{K\lambda}{L \cos \theta}$, where $\lambda$ is the wave length of the x-ray, $2\theta$ is the angle of the diffraction peak, $L$ is the size of the crystallite, and $K$ is the Scherrer constant. Using $K = 0.94$ as an approximation and the FWHM of the (002) peak, we estimate the crystallite size to be ~ 14 nm.

**S3. Variable range hopping fitting to the insulating sample:**

![Figure S2](image)

**Figure S2:** (a) The two-dimensional VHR fitting to the insulating NbSe₂ sample. (b) The three-dimensional VHR fitting. Both of them do not describe the temperature dependence of the resistance.
To clarify that the insulating behavior of the NbSe2 sample grown at high temperature (main text Fig. 2a blue) is not due to localization effect as a result of degradation of the sample quality, we compared the fitting using variable range hopping (VRH) model in both two-dimension and three-dimension cases. As can be seen in Fig. S1, both of the plots \( \ln(R) \) vs. \( T^{-3} \) (2D case) and \( \ln(R) \) vs. \( T^{-4} \) (3D case) could not be fitted by a line. In contrast, Fig. 3c in the main text best describe \( \sigma(T) \) as \( \sigma \sim e^{-\frac{E_0}{k_B T}} \), which indicates that the insulating behavior is due to an energy gap.

**S3. DFT calculations of the phonon spectrum of 1T-NbSe₂:**

![Figure S3: The phonon spectrum of 1T-NbSe₂ calculated by DFT. There are four Raman active modes below 300 cm⁻¹.](image)

While optimizing the electronic structures, the vdW interactions were accounted for using a semi-empirical correction to the Kohn Sham energies also known as Grimme's DFT-D2 approach. For all the electronic structure calculations, a Monkhorst–Pack scheme was used to integrate over the Brillouin zone with a k-mesh of \( 8 \times 8 \times 8 \). A plane-wave basis cutoff of 400 eV was used for all the calculations. All structures were optimized using the BFGS optimizer.
implemented in the Python package atomic simulation environment (ASE).\textsuperscript{5} VASP was used as a force calculator for the optimization. The structures were optimized until the largest force on the atoms was less than $10^{-6}$ eV/Å. The optimized lattice constants for bulk 1T-NbSe$_2$ were $a = 3.60$ Å and $c = 6.36$ Å. ASE was used to programmatically optimize all of the structures as a function of strain. During the optimization, strain was applied equally to lattice constants $a$ and $b$ and kept fixed throughout the optimization. The lattice constant $c$ was allowed to relax. During the cell optimization under strain, the cell shape was also allowed to change, but it remained unchanged. The small displacement method implemented in software package Phonopy was used to calculate the phonon dispersion of the optimized structures.\textsuperscript{6} A converged supercell size of $2 \times 2 \times 2$ was used for all the phonon dispersion calculations.

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