Nb$_2$SiTe$_4$: A Stable Narrow-Gap Two-Dimensional Material with Ambipolar Transport and Mid-Infrared Response

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ABSTRACT: Two-dimensional (2D) materials with narrow band gaps (~0.3 eV) are of great importance for realizing ambipolar transistors and mid-infrared (MIR) detections. However, most of the 2D materials studied to date have band gaps that are too large. A few of the materials with suitable band gaps are not stable under ambient conditions. In this study, the layered Nb$_2$SiTe$_4$ is shown to be a stable 2D material with a band gap of 0.39 eV. Field-effect transistors based on few-layer Nb$_2$SiTe$_4$ show ambipolar transport with a similar magnitude of electron and hole current and a high charge-carrier mobility of ~100 cm$^2$ V$^{-1}$ s$^{-1}$ at room temperature. Optoelectronic measurements of the devices show clear response to an MIR wavelength of 3.1 μm with a high responsivity of ~0.66 AW$^{-1}$. These results establish Nb$_2$SiTe$_4$ as a good candidate for ambipolar devices and MIR detection.

KEYWORDS: Nb$_2$SiTe$_4$ ambipolar transistor, mid-infrared, two-dimensional material, narrow gap, stability

M aterials with narrow band gaps in the range of 0.15 to 0.4 eV are important in the family of semiconductors for their applications in mid-infrared (MIR) detections. Among them, indium arsenide, mercury cadmium telluride, and so on are the most studied and used materials. In addition to these conventional semiconductors, newly developed narrow-gap two-dimensional (2D) materials are also showing great potential in the MIR detections. For example, few-layer black phosphorus (bP) with a band gap of ~0.3 eV has been used to demonstrate high photoresponsivity and detectivity in the MIR range.1–3 When alloyed with arsenide, the band gap of black arsenic phosphorus (bAP) can be further tuned from ~0.3 eV to ~0.15 eV, which extends the spectrum to the long-wavelength infrared.4,5 The layered nature of these materials gives them large flexibility and ease of integration with other materials to form various device structures.5,6,7

In addition to their applications in optoelectronics, narrow-gap 2D semiconductors such as bP can be used as the channel material of field-effect transistors (FET) and support ambipolar transport, in which the majority carriers of the channel can be easily switched between electrons and holes by electrostatic doping of the gate voltage.8,9 This property offers great opportunity for device functions such as field-programmable p–n junctions,10 which are not achievable by conventional semiconductors.

Due to these applications, narrow-gap 2D materials are in high demand. However, most of the 2D semiconductors studied to date have band gaps on the order of 1 eV or higher.11 bP and bAP have suitable band gaps, but these materials degrade within hours under ambient conditions due to the chemical instability of phosphorus.6,12,13 Thus, more stable narrow-gap 2D materials are needed. Herein, we report a layered material, Nb$_2$SiTe$_4$ (NST), with a band gap of 0.39 eV. When few-layer NST is fabricated into an FET, it shows ambipolar transport with similar capability of conducting electrons and holes. A respectable hole mobility of ~100 cm$^2$ V$^{-1}$ s$^{-1}$ at room temperature is obtained. When illuminated by MIR light with a wavelength of 3.1 μm, NST devices demonstrate a high photoresponsivity of ~0.66 AW$^{-1}$. They also show good stability under ambient conditions without any...
forms an angle of 107° with the basal plane (Figure 1f). The orthorhombic structure was resolved with lattice constants of 0.63 and 0.78 nm; these contain two layers. Hence, the layer distance, c = 0.697 nm. For this monoclinic crystal structure, the parameters: V = 0.5 V, I = 100 pA. (g) dV/dI spectra of an NST crystal. Inset is the same data plotted in log scale for a better determination of band edges. The band gap $E_g$ is measured to be 0.39 eV. STS parameters: $V_{\text{initial}} = 0.5 V, I_{\text{initial}} = 100 pA; \text{lock-in frequency } f = 991.2 Hz$, modulation voltage $V_{\text{rms}} = 10 mV$.

encapsulation. These findings demonstrate NST to be a stable narrow-gap 2D material with great application potentials.

**RESULTS AND DISCUSSION**

NST was synthesized decades ago, but there have been few studies about it. Bulk NST crystal belongs to the space group P121/c1 (No. 14), which is in the monoclinic crystal system. Figure 1a to d show the different views of the NST structure (more 3D views can be found in Figure S1 of the Supporting Information). It is a layered material formed by stacking the Te—(Nb, Si)—Te sandwich layers, which bears similarity to the transitional metal dichalcogenides (TMDs) such as MoS$_2$, NbSe$_2$, and so on. The inner atomic layer consists of two types of atoms (Nb and Si) instead of one in the TMDs. The lattice parameters have been determined as $a = 0.63$ nm, $b = 0.79$ nm, $c = 1.47$ nm, $\alpha = 90^\circ$, $\beta = 107^\circ$, and $\gamma = 90^\circ$. We synthesized the NST crystals with the self-flux method (see the Methods section). The as-grown crystals were black, thin flakes with metal luster, and their size was measured in millimeters (inset of Figure 1e). Due to the layered nature, powder X-ray diffraction (XRD) was used to probe the basal planes in the crystal. Sharp Bragg peaks indicated the high quality of our crystals. According to Bragg’s law, $2d \sin \theta = n \lambda$, where $d$ is the layer distance, $\theta$ is the X-ray incident angle, $n$ is the order of a Bragg peak, and $\lambda = 0.154$ nm, the wavelength of the X-ray. For the first peak in Figure 1e, $\theta = 6.34^\circ$ and $n = 1$, which gives $d = 0.697$ nm. For this monoclinic crystal structure, the c axis forms an angle of 107° with the basal plane and the unit cell contains two layers. Hence, $c = 2d / \sin 107\ ^\circ = 1.46$ nm. To complement the XRD study, we used scanning tunneling microscopy (STM), which resolves the atomic structure within the basal plane (Figure 1f). The orthorhombic structure was clearly visible with lattice constants of 0.63 and 0.78 nm; these findings are consistent with values found in the literature.

Figure 1b and f show that the unit cell of NST contains a large number of atoms, which resulted in many phonon modes as shown by Raman spectroscopy (Figure S2 in the Supporting Information). In addition to revealing the atomic structure, more importantly, STM can be used to measure the band structure with the technique of scanning tunneling spectroscopy (STS). In Figure 1g, the Fermi level is located at 0.08 eV above the valence band edge $E_v$, indicating the intrinsic p-type doping. The band gap $E_g$ was determined to be 0.39 eV in the MIR range, which is promising for both ambipolar transport and MIR detection.

To measure the transport property of few-layer NST, the Scotch tape method was adopted to exfoliate NST onto highly p-doped Si substrate covered with 300 nm thermally grown SiO$_2$. Then, electron-beam lithography and metal deposition were used to fabricate the device. A typical FET device is shown in the optical image of Figure 2a. The flake thickness was measured by atomic force microscopy (AFM) to be 7.5 nm (other thicknesses of few-layer NST showed similar behavior). The metal electrodes consisted of 10 nm of Ti and 40 nm of Au. All transport measurements were performed in a vacuum ($\sim 10^{-5}$ mbar) and in the dark with a Janis ST-500 probe station.

The linear two-terminal output curves measured from 300 to 78 K (Figure 2b) indicated that Ti forms good contacts with NST. We determined the work function of NST to be 4.36 eV by ultraviolet photoelectron spectroscopy (Figure S3), which matched well with that of Ti (4.3 eV). To extract the intrinsic field-effect mobility, four-terminal transfer curves were measured as a function of temperature (Figure 2c). The p-type transport was consistent with the band structure measured by STS in Figure 1g. Mobility $\mu$ was calculated by $\mu = \frac{1}{G} \frac{dG}{dV_g}$, where $G$ is the conductance, $V_g$ is the back-gate voltage, $C_{ox} = 1.15 \times 10^{-8}$ F cm$^{-2}$ is the specific capacitance of the gate oxide,
NST has a higher mobility,21,22 which is essential for high-
performance electronic devices. Similar transport properties
among them. With device optimization, such as better
substrates and dielectric screening,23,24 the mobility should
be further improved.

Due to the narrow band gap, it is possible to change the
majority carrier type in the channel from holes to electrons
simply by the back-gate voltage. Figure 3a shows the transfer
curve of a 5.7 nm NST FET (Figure S5), where ambipolar
behavior can be clearly seen. The electron and hole currents
be further improved.

\[ E_g = \varepsilon \left( V_{ds} + \frac{V_{th-n} - V_{th-p}}{\beta_n - \beta_p} \right) \]

(1)

where \( \varepsilon \) is the electron charge, \( V_{ds} \) is the source–drain bias
(100 mV in Figure 3a), \( V_{th-n} \) (\( V_{th-p} \)) is the threshold voltage on
the electron (hole) side, and \( \beta_n \) (\( \beta_p \)) is the gate efficiency in
tuning the band edge on the electron (hole) side, which is
defined below. The threshold voltages are determined from
Figure 3a. The subthreshold swing (SS) of an FET can be
written as26

\[ SS = \ln \left( \frac{1 + \frac{C_d + C_{ox}}{C_{th}}} {1 + \frac{C_p + C_{ox}}{C_{th}}} \right) \ln \frac{kT}{\varepsilon} \beta \]

(2)

where \( k \) is the Boltzmann constant, \( T \) is the temperature (150
K in our case), and \( C_d \) (\( C_p \)) is the depletion (interface)
capacitance. The gate efficiency \( \beta \) is defined as
\( \beta = 1 + \frac{C_d + C_{ox}}{C_{th}} \). The equivalent capacitance circuit is shown
in the inset of Figure 3a. Due to the presence of \( C_d \) and \( C_{ox} \), the
gate voltage \( V_g \) in the subthreshold regime can only cause a
down-scaled shift of the bands in the device. The scaling factor
\( \beta \) can be extracted from the fittings in Figure 3b. Since the
electron side and hole side showed slightly different SS, both
values were used in eq 1. The calculated transport gap of NST
was 0.18 eV, less than the STS value. This difference may have
come from the thermal broadening of the band edges and the
nonuniform doping in the device.

The band gap values of NST measured by STS and transport
indicated that NST devices should have MIR responses. To
test its optoelectronic property, we first used 532 nm laser
pulses to characterize the NST FETs as shown in Figure 4a.

With a source–drain bias of 50 mV, a gate voltage of 0 V, and a
310 \( \mu \)W laser, the device showed \( \sim 1 \) \( \mu \)A of photocurrent and fast response. We defined the rising and falling times as the
time span between 90% and 10% of the total photocurrent,
gave a rising edge of 20 ms and a decaying edge of 310
ms. We note that the dark current was high (\( \sim 7 \) \( \mu \)A) due to
the intrinsic heavy p-type doping. Response to MIR wave-
length (3.1 \( \mu \)m) was also measured as shown in Figure 4b,
with a laser power of \( \sim 160 \) nW. The photocurrent was

Figure 3. (a) Transfer curve of an NST device showing ambipolar
transport. \( V_{th-n} \) and \( V_{th-p} \) represent the threshold voltages on the
electron side and hole side, respectively. Inset: Schematic of
equivalent capacitance model of the device. \( C_d \) and \( C_{ox} \) represent
the depletion layer capacitance and interface capacitance,
respectively. (b) Data from (a) plotted in log scale. Red lines are the linear
fitting curves to extract the subthreshold swings of the electron side (SS\( _n \)) and hole side (SS\( _p \)).

Figure 4. (a) Response to laser pulses with 532 nm wavelength. The rising and falling time is defined in the main text. (b) Response to MIR laser pulses with a 3.1 \( \mu \)m wavelength.
approximately 100 nA, which gave a responsivity of 0.66 A W⁻¹, much larger than the responsivity of bAP. These results demonstrated the potential of NST for MIR detection.

The ambipolar transport and MIR response have shown the application potential of NST. Stability is another important property that should be examined, as it has always been a substantial challenge for narrow band gap semiconductors, such as bP and bAP. These materials tend to react quickly with oxygen and water moisture in air and degrade completely in the time scale of minutes to several hours. Exfoliations of these materials are usually done in gloveboxes with water and oxygen contents less than 1 ppm. Special care during device fabrication and various encapsulation techniques are needed to protect these materials, which brings in extra difficulties and complexities. However, NST showed resistance to ambient conditions. Exfoliation and inspection were all carried out in air. As shown in the transport data in Figure 5a and b, when a fabricated device was stored under vacuum for 120 h, the mobility increased slightly (from black to red curve), due to the desorption of surface contaminant. When exposed to dry air for another 102 h, mobility was slightly decreased with an increase of conductance (green curve), presumably due to the mild oxidation effect from the air. When the device was stored in air with 40% relative humidity for another 120 h, the device still showed good transport behavior (blue curve), with 40% reduction of its mobility. In the inset of Figure 5b, day-to-day variation of the mobility was monitored and the numerical values are presented in the Supporting Information. After exposure to air, the mobility decreased linearly without obvious change of speed when the air was switched from dry to ambient air with moisture, which indicated the key role of oxygen instead of water. As a comparison, bP and bAP devices usually completely lost their electrical conductivity after a few hours’ exposure to moist air. Raman spectra of the same device before and after measurements also revealed the stability of NST (Figure 5c). All the peaks retained their positions and line profiles, and no new peaks could be seen. The decrease in intensity can be ascribed to the surface oxidation of NST. The AFM image (Figure 5d) of the channel after all the characterizations shows the cleanliness and flatness of the flake, compared with the chemically corroded rough surface of bP and bAP. A similar stability can be seen on another device in Figure S6 of the Supporting Information.

CONCLUSIONS

In conclusion, we have explored the layered material Nb₅SiTe₄ as a 2D narrow-gap semiconductor. Ambipolar transport with respectable mobility and comparable electron–hole injection indicates its outstanding electronic property. Good responsibility to MIR wavelength demonstrates the great potential for optoelectronic applications. In addition to these characteristics, its superior stability renders Nb₅SiTe₄ a special position among all the narrow-gap 2D materials, which warrants its further exploration.

METHODS

Crystal Growth. Nb (99.95%, Aladdin Chemicals), Si (99.999%, Aladdin Chemicals), and Te (99.99%, Aladdin Chemicals) powders in a molar ratio of 1:2:8 were mixed using a mortar for 20 min and placed into an alumina crucible. The extra Si and Te were used as the flux for reducing the melting temperature of Nb. The crucible was sealed into a quartz tube under vacuum of 10⁻⁴ Pa and then heated in a high-temperature well-type furnace up to 1150 °C for 15 h. After reaction at this temperature for 5 h, the assembly was slowly cooled to 750 °C at a rate of 1 °C/h and stayed at 750 °C for 15 h. The excess Si and Te were quickly removed from the alumina crucible at this temperature in a centrifuge without breaking the vacuum. Then, the quartz tube was cooled to room temperature in air. Thin pieces of black Nb₅SiTe₄ flakes with metallic luster were obtained in the alumina crucible.

STM and STS. The STM experiments were carried out in the Omicron LT-Qpuls-STM with a tungsten tip calibrated on a Ag(111) surface. To get a clean surface, the NST bulk sample was exfoliated in an ultrahigh vacuum chamber with a base pressure <10⁻⁷ mbar and then transferred to an STM chamber to start the scanning with the base pressure of 10⁻¹¹ mbar and temperature of 77 K.

Device Fabrication and Transport Measurements. All the FET devices in this study were started with NST exfoliation on a highly doped silicon wafer covered with 300 nm of SiO₂. The electron beam lithography was used to design the contacts. Thermal evaporation of electrode metals (10 nm Ti and 40 nm Au) with the lift-off method was used to deposit the contacts. Then, the devices were ready for transport measurement, which was carried out in a Janis ST-500 probe station under vacuum. Keithley source meters 2612B provided the source–drain voltage and gate voltage while measuring the current.

XRD. Powder X-ray diffraction was performed on Nb₅SiTe₄ single crystals aligned along the (001) plane, using a D8 Venture Bruker at room temperature. A Cu Kα source (1.5418 Å) was used.

Raman. A custom-made micro Raman system with ANDOR SR-500i-D2-R spectrometer and 1800 grooves per mm grating was used. The incident laser wavelength was 532 nm.

AFM. All the AFM images were obtained using AFM (Oxford, Cypher S) under ambient conditions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.9b05080.

Additional information showing more 3D views of the crystal from different angles, Raman spectra of different
NST flakes, UPS measurement to obtain the NST work function, transport properties of other few-layer NST FETs, AFM image of the ambipolar device, stability test of another NST device, and a table of mobility values corresponding to Figure 5b (PDF)

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Notes

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