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Bipolar Nb$_3$Cl$_8$ Field Effect Transistors

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Abstract: Field effect transistors based on few-layered van der Waals transition metal halide (TMH) Nb$_3$Cl$_8$ are studied in this work. Few-layered Nb$_3$Cl$_8$ exhibits typical N-type semiconducting behavior controlled by a Si gate, with the electrical signal enhancing as the thickness increases from 4.21 nm to 16.7 nm. Moreover, we find that the tunability of few-layered Nb$_3$Cl$_8$ FETs’ electrical transport properties can be significantly augmented through the use of an ionic liquid gate (or electrical double layer, EDL). This enhancement leads to a substantial increase in the on–off ratio by approximately a factor of $10^2$, with the transfer curve modulated into a bipolar fashion. The emergence of such bipolar tunable characteristics in Nb$_3$Cl$_8$ FETs serves to enrich the electronic properties within the transition metal halide family, positioning Nb$_3$Cl$_8$ as a promising candidate for diverse applications spanning transistors, logic circuits, neuromorphic computing and spintronics.

Keywords: 2D semiconductor; Nb$_3$Cl$_8$; bipolar FETs; electrical double layer

1. Introduction

Inspired by the exfoliation of graphene, the low-dimensional materials especially the two-dimensional (2D) van der Waals (vdW) materials have gained great attention due to their natural atomically thin structure, large surface-to-volume ratio, diverse properties, high carrier mobility, mechanical flexibility, heterostructure engineering capabilities, and environmental stability, promoting to unveil emerging physical phenomena, such as quantum Hall effect [1], fractional quantum Hall effect [2], strong correlation properties [3], catalytic performance [4], optoelectronic performance [5], high thermal conductivity [6], etc. These remarkable attributes make them highly promising for various applications in electronics, optoelectronics, energy storage, sensors, and beyond [7–12]. Since then, 2D semiconductors, such as transition metal dichalcogenides (TMDC) [13–15] and transition metal halogens (TMHs) [16,17], dominated by interlayer weak van der Waals interaction have been extensively investigated. Compared to TMDC materials, TMH materials exhibit more attractive advantages due to their richer magnetic and topological properties [18,19].

Nb$_3$Cl$_8$, as a member of vdW TMHs, is believed to be mechanically exfoliated, with an interlayer cleavage energy of 0.18 Jm$^{-2}$ [20]. Recent study has confirmed the existence of a breathing Kagome lattice in Nb$_3$Cl$_8$, which could open a band gap at the Dirac point due to the spatial inversion symmetry being broken [21]. Due to Nb$_3$Cl$_8$’s structural characteristics, it has also been predicted to manifest quantum spin liquid owing to magnetic frustration [22], yielding a topological flat band (TFB) because of its inherent mirror symmetry. The TFB is then confirmed by using the angle-resolved-photon-energy-spectroscopy (ARPES) with a band gap around 1.12 eV [21]. The magnetic ground state of single layer Nb$_3$Cl$_8$ has also been reported recently [21]. Nb$_3$Cl$_8$, a material that can be mechanical exfoliated down to a single layer, possesses a suitable bandgap as a semiconductor, holds the promise for the low-dimensional material field-effect transistors (FETs), and exhibits...
strong electrostatic control. With its stability at room temperature, non-toxic nature, and other characteristics, Nb\textsubscript{3}Cl\textsubscript{8} is considered a highly promising electronic system for studying electrical transport performance [20]. Recently, attempts have been devoted to probe the electrical properties of few-layered Nb\textsubscript{3}Cl\textsubscript{8}, which is encapsulated by hexagonal-boron nitride (h-BN) [23] and O\textsubscript{2} adatoms [24], respectively. However, the reported on–off ratio of Nb\textsubscript{3}Cl\textsubscript{8} based FETs is around 10\textsuperscript{6}, which greatly limits its application in electronic devices. Therefore, it is imperative and necessary to investigate effective tuning methods to enhance the on–off ratio and enrich the electrical transport characteristics of Nb\textsubscript{3}Cl\textsubscript{8}-based FETs.

In this work, we employ the mechanical exfoliation method to obtain high-quality few-layered Nb\textsubscript{3}Cl\textsubscript{8} nanoflakes and fabricate FETs based on few-layered Nb\textsubscript{3}Cl\textsubscript{8} with different thicknesses. Systematic studies are conducted on the electrical properties for few-layered Nb\textsubscript{3}Cl\textsubscript{8} FETs equipped with Si and EDL gates, respectively. Our results show a N-type doping and on–off ratio of 10\textsuperscript{10} with Si gate FETs, while the devices exhibit bipolar doping effects and on–off ratio over 10\textsuperscript{2} with EDL gates. Our work could shed light on the future investigation on nano-electronic devices based on Nb\textsubscript{3}Cl\textsubscript{8}.

2. Methods

2.1. Manufacture and Testing of FETs

We employ mechanical exfoliation to obtain few-layered Nb\textsubscript{3}Cl\textsubscript{8} from high-quality bulk Nb\textsubscript{3}Cl\textsubscript{8}. Nb\textsubscript{3}Cl\textsubscript{8} nanoflakes are then deposited on SiO\textsubscript{2} (300 nm)/Si\textsuperscript{++} substrate. Morphology and thickness of few-layered Nb\textsubscript{3}Cl\textsubscript{8} are characterized by optical microscopy and atomic force microscopy (AFM) [25]. Then, we further study its stability upon heating and organic solvent compatibility (acetone and isopropanol) for following fabrications. It reveals that heating could cause degradation of Nb\textsubscript{3}Cl\textsubscript{8}. Therefore, we avoid using any heating step for the whole fabrication process, such as the BN-encapsulated process. Next, we fabricate the contact electrode of the Ti5 nm/Au50 nm film by using the electron beam lithography and electron beam evaporation. Finally, we use a semiconductor analyzer (Keysight B1500a) to measure the field effect curves and I-V curves of the as-prepared Nb\textsubscript{3}Cl\textsubscript{8} devices.

2.2. Ionic Liquid Gating Method

We use the ionic liquid N,N-diethyl-N-methyl-N-(2-methoxyethyl) ammonium bis (trifluoromethylsulfonyl) imide (DEME-TFSI) as a gate on the Nb\textsubscript{3}Cl\textsubscript{8} surface to create an EDL. It exhibits great modulation compared with conventional solid dielectric materials [26,27]. A droplet of DEME-TFSI is deposited to cover both the device channel and the gate pads, after which the entire area is covered with a thin glass lid for observation under the microscope [28].

2.3. Raman Spectra

Raman spectra are acquired for both bulk and few-layered Nb\textsubscript{3}Cl\textsubscript{8} using a 532 nm excitation source. The experiments to investigate the layer-dependent Raman behavior are conducted using a confocal microscope Raman spectrometer (LabRAM HR Evolution, Horiba Scientific, Raman detector, Lille, France) in a backscattering geometry. The emitted Raman signals are collected and dispersed by a 1800 gr/mm grating, with a 532 nm laser serving as the excitation source. The laser beam was focused onto exfoliated Nb\textsubscript{3}Cl\textsubscript{8} flakes using a 100× objective (NA = 0.9, WD = 0.21 mm), resulting in a spot size of approximately 1 \mu m. Each Raman spectrum was obtained by averaging ten measurements, with an integration time of 2 s for each spectrum.

3. Results and Discussion

Figure 1a,b show the ball-and-stick schematic diagram of the Nb\textsubscript{3}Cl\textsubscript{8} at the top and side views. The green and blue balls represent Nb and Cl atoms, respectively. The structure belongs to the space group P\textsubscript{3}m\textsubscript{1}. The gray dash lines identify the trimer clusters combined by Nb atoms. The short distance between Nb-Nb is d\textsubscript{1} = 2.8 Å and the long one is d\textsubscript{2} = 3.9 Å.
The large trimer clusters and the small ones alternative arrangement forms the breathing Kagome lattice. The optical microscopy image of a typical exfoliated multi-layered Nb$_3$Cl$_8$ is shown in Figure 1c, where we can see clearly the optical contrast between different layers. AFM scanning helps us to confirm the height difference between layers, where the thinnest part is detected to be about 1.3 nm with about two layers. Therefore, the 2D van der Waals nature is confirmed by both optical microscopy and AFM.

Figure 1. Structural properties of layered Nb$_3$Cl$_8$. The ball-and-stick schematic diagram of the Nb$_3$Cl$_8$ at top view (a) and side view (b), respectively. (c) Optical microscopy image of a typical multi-layered Nb$_3$Cl$_8$ exfoliated on the SiO$_2$ (300 nm)/Si$^{++}$ substrate. (d) The AFM morphology mapping of the region marked in white in (c). (e) Height profile along white dash line in (d). The height for the steps are marked in the figure, where the thinnest region is estimated to be 0.98 nm. (f) Raman spectra for exfoliated Nb$_3$Cl$_8$ with thickness from the bulk 340 nm to 1.3 nm.

$I$-$V$ curves of a typical thin-layer Nb$_3$Cl$_8$ device with gate voltage varying from $-50$ to $50$ V are shown in Figure 2a, while its optical microscopy image is shown in the inset. Non-linear $I$-$V$ curves are obtained by varying the drain voltage in between $\pm 1$ V, which means a non-ohmic contact is formed between Nb$_3$Cl$_8$ and electrodes. By increasing the gate voltage gradually from $-50$ to $+50$ V, the absolute value of $I_{ds}$ is increasing. Fixing the $V_{ds}$ constantly at $+1$ V, by changing Si gate voltage from $-50$ to $+50$ V gradually, the field-effect curves are obtained and shown in Figure 2b. Combing transfer curves shown in Figure 1a,b, the intrinsic N-type semiconductor of thin-layer Nb$_3$Cl$_8$ device can be confirmed, which is consistent with the previous work [24]. Compared with the transfer curves for devices at different thickness in Figure 2b, we can find that increasing thickness of Nb$_3$Cl$_8$ could play a positive role to give rise to $I_{ds}$. This phenomenon could be attributed to an improved contact and/or a channel conductivity enhancement. The field-effect curves exhibit similar trends for each thickness devices, and the on-off ratio is approximately consistent. This indicates that the electrical modulation of the material remains relatively stable across the range of thicknesses from 4.21 to 16.7 nm tested in this experiment.

Non-linear $I$-$V$ behavior in Figure 2a indicates that there may exist a high contact resistance between the Nb$_3$Cl$_8$ thin layer and the Ti/Au electrodes. This resistance could impede the Si gate’s modulation to the sample’s intrinsic carriers. Therefore, we measure the resistance between the two middle electrodes using both two-probe and four-probe methods. As shown in Figure 3a, the two-probe measurement shows a non-linear $I$-$V$ curve and a changing resistance with different $V_{ds}$ due to the Schottky barrier between the electrode and the Nb$_3$Cl$_8$ channel. The red curve in Figure 3a shows that the total resistance ($R_{tot} = \frac{dV_{ds}}{dI_{ds}}$) is about 25 M$\Omega$, which is composed of the Nb$_3$Cl$_8$ channel resistance
(R_{ch}) and the contact resistance (R_c). Then, we select a safe input current range from −20 to 20 nA for the four-probe measurement, preventing an excessive voltage causing the device breakdown. A linear V-I curve and a stable resistance in Figure 3b shows that the channel intrinsic resistance ($R_c = dV_{23}/dI_{14}$) of Nb$_3$Cl$_8$ is about 14 MΩ. The contact resistance ($R_c$) is then calculated to be about 10 MΩ, which is of the same order as the channel resistance. Therefore, resistance obtained by the four-probe method compared to the two-probe method (Figure 3c) demonstrates a more accurate field effect of the Nb$_3$Cl$_8$ flake.

![Figure 2](image.png)

**Figure 2.** (a) I-V curves of a typical transistor with Si gate voltage varying from −50 to 50 V. The inset in upper left shows the optical microscopy of the tested devices fabricated on the SiO$_2$ (300 nm)/Si++ substrate. (b) Field-effect curves with thickness of Nb$_3$Cl$_8$ ranging from 4.21 to 16.7 nm, where the $V_{ds}$ is fixed at +1 V.

Since the limited tuning effect of the solid Si gate, we then turn to a stronger tuning method by using the ionic liquid to create a non-volatile but hygroscopic EDL [29]. A field effect transistor with 16.7 nm Nb$_3$Cl$_8$ is prepared here for ionic liquid tuning. The transistor’s optical image and schematic diagram are shown in Figure 4a,b. The transfer curves under ionic liquid with different $V_{ds}$ are shown in Figure 4c, which exhibits a stronger tuning effect compared with solid Si gate shown in Figure 2b. Without external doping, the Nb$_3$Cl$_8$ exhibits an intrinsic N-type semiconductor, which is consistent with the results shown in Figure 2b. Tuned by the ionic liquid, Nb$_3$Cl$_8$ shows bipolar semiconductor characters, where the dominated carrier type could be changed by varying the voltage applied on the ionic liquid. Take the transfer curve at $V_{ds} = 0.1$ V, for example, when the gate voltage applied on the ionic liquid increases from −0.7 to 1.5 V, negative carriers (electrons) accumulates in Nb$_3$Cl$_8$ channel and $I_{ds}$ increases responsively, showing a N-type field effect. When the gate voltage decreases from −0.7 to −1.5 V, positive carriers (holes) take in charge, showing a P-type field effect. Besides the bipolar FET characters, the on–off ratio could be further enlarged by a factor of $10^2$ compared with the solid Si gated FET, which conforms again the strong doping ability of EDL. The corresponding $I_{ds}$ could be further increased by increasing the $V_{ds}$, which can be observed obviously in Figure 4c. The bipolar characters and enhanced on–off ratio under EDL are further conformed by checking additional FETs with varying thickness (12.4 and 6.08 nm) of Nb$_3$Cl$_8$. 
Figure 3. (a) I-V curve and total resistance acquired by two-probe testing method. (b) V-I curve and corresponding channel resistance are measured through four-probe testing method. The inset is the schematic illustration of four-probe measurement. (c) The field effect of the $V_{gs}$ on the total resistance ($R_{tot}$) and channel resistance ($R_{ch}$).

Figure 4. Optical microscopy image (a) and schematic diagram (b) of the Nb$_3$Cl$_8$ FET with ionic liquid. (c) Field-effect curves of 16.7 nm Nb$_3$Cl$_8$ FET with $V_{ds}$ at 0.1, 0.2, 0.5, and 0.8 V under an ionic liquid tuning, respectively.
4. Conclusions

By using the mechanical exfoliation method, the high-quality few-layered TMH material Nb$_3$Cl$_8$ is acquired. Systemically electronic properties are studied by fabricating the Nb$_3$Cl$_8$-based FETs. By applying the solid Si gate and ionic liquid doping methods, the intrinsic N-type semiconductor characters are discovered. Furthermore, the implementation of the ionic liquid results in the formation of an electric double layer at the surface of the Nb$_3$Cl$_8$ channel, inducing the bipolar characteristics in Nb$_3$Cl$_8$-based FETs. This enhancement is evidenced by the significant increase in the on–off ratio, rising from approximately $10^0$ with Si gating to around $10^2$ with ionic liquid tuning. The effectiveness of our ionic liquid in achieving this tuning effect was further verified by examining Nb$_3$Cl$_8$ FETs with varying thicknesses. Considering the reported electronic performances and light absorption properties, our findings present new possibilities for future electronic studies involving Nb$_3$Cl$_8$. Moreover, these results may provide valuable insights that can be extrapolated to other TMH materials.

Author Contributions: Y.L., B.D., K.Z. and T.Z. conceived the research; Y.L. exfoliated sample and fabricated FETs; Y.L. and T.Z. measured the devices’ field effect curves with EDL; writing—original draft preparation, Y.L.; writing—review and editing, B.D., T.Z. and K.Z.; All authors contributed to the discussion of the data. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (NSFC) with Grant No. 12374185, U21A6004, 12204287, 62204145.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

Acknowledgments: L.Y.X. acknowledges the great support from Zheng Vitto Han for fruitful discussion, supervision of Wu Zhou and Junfeng Gao.

Conflicts of Interest: The authors declare no conflicts of interest.

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