Edge Defect-Free Anisotropic Two-Dimensional Sheets with Nearly Direct Band Gaps from a True One-Dimensional Van der Waals Nb$_2$Se$_9$ Material

Weon-Gyu Lee, You Kyoung Chung, Junho Lee, Bum Jun Kim, Sudong Chae, Byung Joo Jeong, Jae-Young Choi,* and Joonsuk Huh*

Cite This: ACS Omega 2020, 5, 10800−10807

ABSTRACT: Dangling-bond-free two-dimensional (2D) materials can be isolated from the bulk structures of one-dimensional (1D) van der Waals materials to produce edge-defect-free 2D materials. Conventional 2D materials have dangling bonds on their edges, which act as scattering centers that deteriorate the transport properties of carriers. Highly anisotropic 2D sheets, made of 1D van der Waals Nb$_2$Se$_9$ material, have three planar structures depending on the cutting direction of the bulk Nb$_2$Se$_9$ crystal. To investigate the applications of these 2D Nb$_2$Se$_9$ sheets, we calculated the band structures of the three planar sheets and observed that two sheets had nearly direct band gaps, which were only slightly greater (0.01 eV) than the indirect band gaps. These energy differences were smaller than the thermal energy at room temperature. The 2D Nb$_2$Se$_9$ plane with an indirect band gap had the shortest interchain distance for selenium ions among the three planes and exhibited significant interchain interactions on the conduction band. The interchain strain induced an indirect-to-direct band gap transition in the 2D Nb$_2$Se$_9$ sheets. These 2D sheets of Nb$_2$Se$_9$ with direct band gaps also had different band structures because of different interactions between chains, implying that they can have different charge mobilities. We expect these dangling-bond-free 2D Nb$_2$Se$_9$ sheets to be applied in optoelectronic devices because they allow for nearly direct band gaps. They can also be used in mechanical sensors because the band gaps can be controlled by varying the interchain strain.

INTRODUCTION

Two-dimensional (2D) van der Waals materials, including graphene and transition-metal dichalcogenides (TMDCs) such as MoS$_2$ or black phosphorus, have planar crystalline structures held together by strong in-plane interactions and weak van der Waals out-of-plane interactions. They can be metallic like graphene,$^{2,7}$ semiconducting like MoS$_2$ or black phosphorus,$^{8-12}$ or insulating like boron nitride.$^{13}$ They have no dangling bonds on their surface.

These semiconducting TMDCs can exhibit an indirect-to-direct band gap transition, which is possible via dimensional reduction. A semiconductor with a direct band gap can absorb photons without being disturbed by phonons and can thus exhibit excellent photoluminescence. Tuning of the band gap via strain,$^{14-17}$ changing the number of 2D sheets,$^{18-21}$ application of electric fields, or interactions with other compounds$^{9,15,17,22}$ can introduce indirect-to-direct band gap transitions in various 2D TMDCs. Materials for which the energy difference between the direct and indirect band gaps is less than the thermal energy of room temperature can be considered “nearly direct band gap” materials, which can also exhibit strong light absorption.$^{23,24}$

Conventional materials (i.e., not van der Waals 2D materials) have dangling bonds on 2D surfaces that act as scattering centers when charge carriers move, and this disturbs their mobilities.$^{25}$ Likewise, van der Waals 2D materials have dangling bonds on their edges. By reducing the dimensionality to a one-dimensional (1D) structure, the edge defects in van der Waals materials can be removed, resulting in fewer defect structures. 1D van der Waals materials have chain crystalline structures with strong intrachain chemical bonds, and these chains are stacked via weak van der Waals interchain interactions in their bulk crystals. These materials show unusual physical phenomena, including superconductor−insulator transitions,$^{26,27}$ charge density waves,$^{26,28}$ topological insulating properties,$^{29,30}$ electron field emissions,$^{31}$ ultralong ballistic phonon transfer,$^{32}$ and molecular-scale conductivity.$^{33}$ They can be used to induce the thermoelectric effect$^{34,35}$ and in field-effect transistors due to their high charge carrier...
V2Se9 chains have direct band gaps, while bulk Nb2Se9 and tellurium, Mo3S, and TaSe3, ZrSe3, NbSe3, etc., have indirect band gaps.59,60 True 1D van der Waals materials with purely van der Waals interactions, including transition-metal trichalcogenides (TiS3, TaSe3, ZrSe3, NbSe3, etc.), bismuth-rich iodides Bi4I9 (x = 4, 14, 16, 18), Nb2PdSe9, Ta2Pd3X8 (X = S, Se), Sb2Se3, and CsBi4Te6. True 1D materials with purely van der Waals interactions are rare, but more effectively address the dangling bond problem. These materials include hexagonal tellurium, Mo3S, I4, and VS6. Novel true 1D van der Waals materials, Nb2Se9 and V2Se9,51–56 have been synthesized and exfoliated to create nanowires, nanoribbons, and molecular chains by mechanical and liquid exfoliations.57,58 Band structure calculations performed using density functional theory (DFT) have revealed that bundles of 1D Nb2Se9 and V2Se9 chains have direct band gaps, while bulk Nb2Se9 and V2Se9 crystals have indirect band gaps.59,60 True 1D van der Waals materials can form a highly anisotropic 2D plane, which has the chemical bond along 1D chains and van der Waals interactions across the chains. The resulting 2D sheets have no dangling bonds on their edges. Thus, a 2D sheet consisting of a true 1D van der Waals material can be used to make transistor devices with small scales that are free from the dangling bond problem. Additionally, in the case of a 2D layer of tellurium that is composed of 1D nanochains, the noncovalent interaction between chains can affect the characteristics of the 2D layer. This makes the charge carrier mobility and optical absorption along the noncovalent bonded direction (cross-chain) stronger than those along the covalent bonded direction.64 Recently, 2D sheets of Nb2Se9 consisting of aligned 1D chains have been successfully prepared by mechanical exfoliation,61,62 thus adding another class of 2D materials, that is, dangling bond-free 2D materials, to the currently existing 2D materials.

To determine the capabilities of these dangling bond-free highly anisotropic 2D materials, we calculated the band structures of 2D Nb2Se9 sheets. Three 2D sheets with distinct band structures were composed from the bulk structures. We observed that two 2D sheets had nearly direct band gaps of 1.18 and 1.17 eV, which could be activated by thermal energy at room temperature, and one 2D sheet had an indirect band gap of 0.84 eV. Charge density analysis showed that the interchain interactions between selenium atoms determined the energy of the band gap of 2D Nb2Se9; thus, (010) plane with interchain bonding had the lowest band gap energy. We varied the interchain distances to investigate the effect of interchain strain on the three 2D sheets and found appropriate extensions of the interchain distances to create direct band gaps in the 2D sheets. Having the nearly direct band gap of Nb2Se9 sheets could be applied to optoelectronic devices, and the response of these sheets to strain could be useful in their application as mechanical sensors.

**RESULTS AND DISCUSSION**

**Atomic Structures.** The initial structure of Nb2Se9 was taken from the Material Database.65 The unit cell has four niobium cations and 18 selenium anions, forming a chain structure. This chain structure is located on the diagonal of the cell in the reference. We selected the [100], [010], and [111] direction vectors in the reference cell as the new lattice vectors and set the length of the chain to be parallel to the [001] direction in the rotated cell.

Figure 1 shows the 2D planes formed by arranging 1D Nb2Se9 chains. Figure 1a shows bulk Nb2Se9 from three different directions along the length of the chain. Because of the hexagonal stacking of the chain, there are three different planes, (010), (100), and (110), made by repeating the single chain unit along [100], [010], and [110], respectively.

The lengths of the optimized cell lattice of the (010) plane are a = 8.16, b = 23.7, and c = 13.0 Å, with vacuum space 15 Å in the lattice vector a. Those of the (100) plane are a = 27.7, b = 8.36, and c = 13.0 Å, with vacuum space 20 Å in the lattice vector a. Those of the (110) plane are a = 11.3 Å, b = 29.3 Å, and c = 13.0 Å, with vacuum space 20 Å in the lattice vector b. In the optimized 2D planes, the interchain distance was 6.85 Å in the (010) plane and 7.17 Å in the (100) and (110) planes (Figure 1). This implied that the interactions between the chains along [010] were the strongest, and it showed that the (010) plane has the minimum band gap. In the bulk, the interchain distances were 6.81, 7.15, and 7.30 Å in the (010), (100), and (110) planes, respectively. The interchain distances in the 2D sheets and bulk were very similar in the (010) and (100) planes. On the other hand, the interchain distance in the (110) 2D plane was smaller than that of the bulk. From the optimization, the (010) plane is most stable, and the other planes have 0.21 eV higher energy than the (010) plane. We confirmed the stability of the planes with their phonon band structures (Figure S3).

**Band Structures.** Figure 2 shows the band structures of the bulk, three 2D Nb2Se9 samples, and single chain of Nb2Se9. All of the 2D structures have indirect band gaps. The (010) plane has the smallest band gap, and the (110) plane has the largest band gap. The indirect band gap of the (010) plane (0.84 eV) is significantly smaller than its direct band gap (0.90 eV). However, the indirect band gaps of 1.16 eV for the (100)
and (1̅10) planes are close to their direct band gaps (1.18 and 1.17 eV, respectively). The differences between the indirect and direct band gaps in these planes are approximately 0.01 eV, which is approximately three times smaller than the thermal energy at room temperature. Thus, the direct band gaps of these two planes can be activated by thermal energy at room temperature. The band gap of the (010) plane (0.84 eV) is close to the band gap of the bulk structure (0.63 eV). The band gaps of the other planes are similar to the band gap of a single-chain structure (1.23 eV).

As shown in Figure 2, the three band structures of the 2D sheets have many peaks and valleys, but the band structure of a single chain shows almost flat lines. However, these peaks and valleys of the 2D sheets have different properties compared to those of the band structures of the bulk. Interestingly, these results show that the structure with a similar band gap has similar band shapes. The valence band (VB) of the bulk has a global maximum at point X in Figure 2 with large differences between the other local maxima. On the other hand, the VBs of 2D Nb₂Se₉ sheets have many local maxima with similar energies. In the (010) plane, all of the local maxima of the VB are global maxima, and the momentum of the global minimum of the conduction band (CB) is different from the momentum of the global maxima of the VB. The depth of the valley of the global minimum of the CB is significant. Thus, the (010) plane has a distinct indirect band gap. In the (100) and (1̅10) planes, the local maxima of the VB have differences of ∼0.01 eV. The VB energy at the wave vector where the CB energy is the global minimum is not the global maximum, but instead a local maximum. Therefore, these planes have nearly direct band gaps.

The three 2D Nb₂Se₉ sheets have different interchain distances and orientations. To determine the reason behind the appearance of distinct band structures in these planes, we changed the interchain distances of the (100) and (1̅10) planes to the interchain distance of the (010) plane. Figure S4 shows the band structures of these 2D sheets when optimized with a fixed lattice cell to achieve the same interchain distance as that of the (010) plane. The band gaps of the (100) and (1̅10) planes decrease slightly because the interchain distance decreases. However, the band gaps of those two planes are still significantly different from the band gap of the (010) plane. The shapes of the band structures of the (100) and (1̅10) planes are almost the same as the band structures with the original interchain distance. This implies that the orientation of the chains has more influence on the band structures of 2D Nb₂Se₉ sheets than the interchain distance.

**Orbital Analysis.** Figure 3 shows the partial density of states (PDOS) of the 2D Nb₂Se₉ sheets. The contribution of the d orbitals of niobium is dominant near the edge of the VB maximum (VBM) region; however, in the CB minimum (CBM) region, the contribution of the p orbitals of selenium is dominant as shown in Figure 3. These results are same as our previous work for bulk and single-chain of Nb₂Se₉.⁵⁹ The PDOS of the (010) plane is different from the other planes. The peaks of Se p orbital at 0−2 eV and the peaks of Nb d orbitals...
orbital at 2–4 eV in the (010) plane have similar height respectively, but the peaks are inclined to lower energy in the other planes. This implies that the electronic characteristics of (010) plane is distinct from the other two planes. Figure S5 shows the contributions of the VB and CB energies at point X and the point (0.242, 0, 0) in reciprocal space (called $T$) relative to the minimum energy on the CB. The CB energy is primarily affected by the selenium $p$ orbitals, and the VB energy is primarily affected by the niobium $d$ orbitals. We analyzed the CB energy at points $X$ and $T$ according to the types of orbitals. At point $X$, the $p_x$ and $p_z$ orbitals were dominant. However, the $p_y$ orbitals were dominant at point $T$. The $p_z$ orbitals were located across the chain; thus, these orbitals were sensitive to the interchain interactions in the (010) plane. The other $p$ orbitals were relatively unaffected by these interactions. The difference in band structures between the 2D Nb$_2$Se$_9$ sheets and single-chain band structures of Nb$_2$Se$_5$ is attributed to the difference in interactions due to the orientation.

The partial charge densities of the VB and CB are shown in Figure 4. In the VBM, niobium $d$ orbitals are dominant and all planes have $\sigma$ bonds between niobium $d$ orbitals on an octahedron. The niobium $d$ orbitals on different octahedrons do not overlap. However, the (100) plane has more delocalized $d$ orbitals and two $\sigma$ bonds that are closer than those of the other planes. In the CBM, selenium $p$ orbitals are dominant, whereas niobium $d$ orbitals contribute little contribution. The (010) plane has a small distribution of selenium $p$ orbitals on one of two octahedrons in a single cell, but the other planes have similar distributions of selenium $p$ orbitals on all octahedrons. The (010) plane also has interchain $\sigma$ bonds between selenium $p$ orbitals on one of the $Se_5$ bridges and one of the selenium octahedrons, but the other planes have no interchain bonds. Therefore, the (010) plane has a more delocalized distribution than the other planes. The (110) plane has a similar charge distribution to the (010) plane for the VB, but it has a similar charge distribution to the (100) plane for the CB. The shortest interchain distances between selenium ions of an octahedron and the bridge are 3.167 ($Se_{13}$–$Se_{18}$), 3.591 ($Se_{11}$–$Se_{10}$), and 3.594 ($Se_{8}$–$Se_{9}$) Å in the (010), (100), and (110) planes, respectively. Although the charge densities in $Se_{11}$–$Se_{10}$ pair in the (100) plane and $Se_{8}$–$Se_{9}$ pair in the (110) plane have $\pi$-bond orientations, their far interion distances make these interactions insignificant [$Se_5$ bridge and octahedron Nb$_2$Se$_5$ are displayed in Figure 4c].

This means that the interchain interactions between the selenium ions of an octahedron and the bridge are strongest in the (010) plane. Although the (100) and (110) planes have shorter interchain distances 3.258 and 3.259 Å between the selenium ions in the $Se_5$ bridges, respectively, the orbital orientation of these two selenium ions is not proper to interact [Figure 4d,f]. Additionally, the selenium ions that exhibit minimal charge distribution in the (010) plane are placed at a longer distance from the $Se_5$ bridge in another chain. The asymmetric arrangement of selenium atoms between two octahedrons in the (010) plane is due to the different interactions between $Se_5$ bridges in another chain. The interchain interactions of the CB in the (010) plane stabilize the energy of the CB and narrow the band gap compared to the other planes. A partial orbital analysis of the CB indicates that the (010) plane has quasi-1D characteristics while the other two planes have true 1D characteristics.

Effect of Interchain Distance. We investigate the effect of interchain strain on the band gaps of the 2D Nb$_2$Se$_9$ sheets in an effort to tune the band gaps of these 2D sheets, especially for the indirect-to-direct band gap transition. We add a relative distance of 10% to the lattice vectors (a value that lies between the separation of chains in the 2D structures) until the difference between a direct band gap and indirect band gap is less than 0.01 eV. Figure 5 shows the differences between the indirect and direct band gaps of 2D sheets with various interchain distances. Here, the (110) plane exhibits a direct band gap with a 10% elongation of the interchain distance. Among the three planes, 10% elongation of the interchain distance is the smallest elongation required to achieve a direct band gap. The (100) plane needs larger elongation to get a direct band gap which is a 50% elongation of the interchain distance. Although the band gap sizes are almost the same as in the original (100) and (110) plane, the response to the elongation is drastically different.
The band structure of the (010) plane with a 30% elongation and the (100) plane with a 50% elongation have the peaks and valleys. Some of the peaks and valleys flipped. Thus, the shape of band structure approaches the band structure of the single chain (Figure S6). However, the band structure of the (1̅10) plane with a 10% elongation is still in an intermediate state between the those of the bulk and a single chain. The effective masses of the electrons and holes are defined by the curvature of the CB at the energy minimum and that of the VB at the energy maximum. Therefore, the effective masses of the (010) and (100) planes with the direct band gaps achieve by minimum strain is similar to those of a single chain, but the effective mass of the (1̅10) plane is different. This implies that the 2D sheets that have direct band gaps induced by strain can have different charge mobility characteristics.

The energies of the indirect and direct band gaps in the (010) plane change significantly. However, the energy difference between the indirect and direct band gaps in the original structure is large; thus, a large strain is required to achieve a direct band gap in the plane. The energy difference between the indirect and direct band gaps in the original (100) plane is small. However, the energies of the indirect and direct band gaps in this plane are weakly affected by the strain; thus, a large strain is also needed to achieve a direct band gap in this plane. The plane (1̅10) shows intermediate characteristics between the (010) and (100) planes. Therefore, the energy difference between the indirect and direct band gaps is small, and the energies of the indirect and direct band gaps are greatly affected by the strain. The (110) can thus be modified to achieve a direct band gap with the smallest elongation.

**CONCLUSIONS**

We constructed three distinct highly anisotropic 2D sheets, (010), (100), and (1̅10) planes, without dangling bonds out of the 1D van der Waals material Nb2Se9 and calculated their atomic and electronic structures. The (010) plane had an indirect band gap of 0.84 eV, and the (100) and (1̅10) planes had nearly direct band gaps of 1.18 and 1.17 eV, respectively. The differences between the indirect and direct band gaps were about 0.01 eV in these two planes. The band structures of the three planes had intermediate features between those of bulk and single-chain Nb2Se9. When the same interchain distance was applied for all three planes, they retained their band structural shapes with small changes in band gap energies. The partial charge densities showed that the (100) plane had the most delocalized electron distribution on the VB along the chain length among the three planes. However, the (010) plane exhibited interchain bonding on the CB caused by the close distance between interchain selenium ions in an octahedron and the Se5 bridge. Thus, the partial charge of the (100) and (1̅10) planes in Nb2Se9 was similar to the partial charge of the 1D chain of Nb2Se9, but that of the (010) plane was different. We were able to obtain quasi-1D characteristics and true 1D characteristics from Nb2Se9 material by modifying...
the direction of chain arrangement. Furthermore, we changed the interchain distance of the three Nb$_2$Se$_9$ planes until a direct band gap appeared. Direct band gaps were observed when the interchain distances increased by 30, 50, and 10% for the (010), (100), and (110) planes, respectively. The band structures of the (010) and (100) planes could be stretched to have a direct band gap similar to that of single-chain Nb$_2$Se$_9$. However, the stretched (110) plane showed a direct band gap while maintaining the band structure of the 2D Nb$_2$Se$_9$ sheet. We expect that these 2D Nb$_2$Se$_9$ sheets can be applied to optoelectronic devices due to their nearly direct band gap. The change in band structures based on the orientation of planes and strain can be used to tune the electronic properties of Nb$_2$Se$_9$ planes. The indirect-to-direct band gap transition via strain can be applied for mechanical sensors. 35 2D Nb$_2$Se$_9$ sheets that are free from dangling bonds can be used to address the problem of scaling down spatial dimensions in semiconductor devices.

**COMPUTATIONAL DETAIL**

Optimized atomic structures and band structures were obtained using the projected augmented wave method implemented in the Vienna ab-initio simulation package (VASP). The Perdew–Burke–Ernzerhof (PBE) exchange–correlation function was applied. The shape of the band structure of bulk Nb$_2$Se$_9$ from HSE06 functional is similar to this from PBE functional (Figure S1). We sampled k-points centered on Γ points. We used a 10 × 1 × 10 k-mesh in the (010) and (110) planes and a 1 × 10 × 10 mesh in the (100) plane for the optimization. Band structures were calculated along the high symmetric path of triclinic symmetry, and each line between high symmetric points are divided into 32 points. The energy cutoff is 520 eV. Tetrahedron smearing with Blochl correction is used in optimization. Projector-augmented wave pseudopotential is adopted. The self-consistent field convergence criterion was $10^{-8}$ eV, and the criterion of the electronic structure optimization was that the forces on the atoms were less than 0.01 eV/Å. We tested dispersion correction methods to consider the effect of the van der Waals interactions between the chains and decided to add the DFT-D3 dispersion energy, as in a previous study. A comparison of the dispersion correction methods applied to the Nb$_2$Se$_9$ bulk structure is given in the Supporting Information (Table S1). The spin–orbit coupling does not affect to the shape of the band structures; thus, we did not include this factor (Figure S2).

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00388.

Additional band structures, phonon band structures, and analysis of the population of orbitals (PDF)

**AUTHOR INFORMATION**

Corresponding Authors

Jae-Young Choi — SKKU Advanced Institute of Nanotechnology (SAINT) and School of Advanced Materials Science & Engineering, Sungkyunkwan University, Suwon 16419, Republic of Korea; Email: jy.choi@skku.edu

Joonsuk Huh — Department of Chemistry and SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, Suwon 16419, Republic of Korea; orcid.org/0000-0002-8792-5641; Email: joonsukhuh@skku.edu

**Authors**

Weon-Gyu Lee — Department of Chemistry, Sungkyunkwan University, Suwon 16419, Republic of Korea

You Kyoung Chung — Department of Chemistry, Sungkyunkwan University, Suwon 16419, Republic of Korea

Junho Lee — Department of Chemistry, Sungkyunkwan University, Suwon 16419, Republic of Korea

Bum Jun Kim — SKKU Advanced Institute of Nanotechnology (SAINT), Sungkyunkwan University, Suwon 16419, Republic of Korea

Sudong Chae — School of Advanced Materials Science & Engineering, Sungkyunkwan University, Suwon 16419, Republic of Korea

Byung Joo Jeong — School of Advanced Materials Science & Engineering, Sungkyunkwan University, Suwon 16419, Republic of Korea

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c00388

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This research was supported by the Nano Material Technology Development Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science, and Technology (NRF-2019R1A6A1A10073079, NRF-2020R1A2C2010984). J.H. acknowledges the support of the POSCO Science Fellowship of the POSCO TJ Park Foundation. We thank Dr. Dongchul Sung for giving valuable comments and guidelines to this paper.

**ABBREVIATIONS**

TMDCs, transition-metal dichalcogenides; DFT, density functional theory; VASP, Vienna ab-initio simulation package; PBE, Perdew–Burke–Ernzerhof; PDOS, partial density of states; VB, valence band; VBM, valence band maximum; CB, conduction band; CBM, conduction band minimum

**REFERENCES**

(1) Son, Y.-W.; Cohen, M. L.; Louie, S. G. Half-metallic graphene nanoribbons. Nature 2006, 444, 347–349.
(2) Avouris, P.; Chen, Z.; Perebeinos, V. Carbon-based electronics. Nat. Nanotechnol. 2007, 2, 605–615.
(3) Xiao, J.; Long, M.; Zhang, X.; Zhang, D.; Xu, H.; Chan, K. S. First-Principles Prediction of the Charge Mobility in Black Phosphorus Semiconduct Nanoribbons. J. Phys. Chem. Lett. 2015, 6, 4141–4147.
(4) Liu, H.; Neal, A. T.; Zhu, Z.; Luo, Z.; Xu, X.; Tománek, D.; Ye, P. D. Phosphorene: An unexplored 2D semiconductor with a high hole mobility. ACS Nano 2014, 8, 4033–4041.
(5) Radisavljevic, B.; Radenovic, A.; Brivio, J.; Giacometti, V.; Kis, A. Single-layer MoS$_2$ transistors. Nat. Nanotechnol. 2011, 6, 147–150.
(6) Late, D. J.; Huang, Y.-K.; Liu, B.; Acharya, J.; Shiordkar, S. N.; Luo, J.; Yan, A.; Charles, D.; Waghmare, U. V.; Dravid, V. P.; Rao, C. N. R. Sensing Behavior ofAtomically Thin-Layered MoS$_2$ Transistors. ACS Nano 2013, 7, 4879–4891.
(7) Kawamura, H.; Shirotani, I.; Tachikawa, K. Anomalous superconductivity in black phosphorus under high pressures. Solid State Commun. 1984, 59, 879–881.
(8) Tsai, M.-L.; Su, S.-H.; Chang, J.-K.; Tsai, D.-S.; Chen, C.-H.; Wu, C.-I.; Li, L.-J.; Chen, L.-J.; He, J.-H. Monolayer MoS₂ heterojunction solar cells. ACS Nano 2014, 8, 8317–8322.

(9) Ryoo, J.; Kim, Y. S.; Santosh, K. C.; Cho, K. Monolayer MoS₂ Bandgap Modulation by Dielectric Environments and Tunable Bandgap Transistors. Sci. Rep. 2016, 6, 29184.

(10) Frindt, B. F. Superconductivity in Ultrathin NbSe2 Layers. Phys. Rev. Lett. 1972, 28, 299–301.

(11) Warschauer, D. Electrical and optical properties of crystalline black phosphorus. J. Appl. Phys. 1963, 34, 1853–1860.

(12) Gibertini, M.; Marzari, N. Emergence of One-Dimensional Wires of Free Carriers in Transition-Metal-Dichalcogenide Nanostructures. Nano Lett. 2015, 15, 6229–6238.

(13) Zhang, K.; Feng, Y.; Wang, F.; Yang, Z.; Wang, J. Two dimensional hexagonal boron nitride (2D-hBN): synthesis, properties and applications. J. Mater. Chem. C 2017, 5, 11992–12022.

(14) Johari, P.; Shenoy, V. B. Tuning the Electronic Properties of Semiconductor Transition Metal Dichalcogenides by Applying Mechanical Strains. ACS Nano 2012, 6, 5449–5456.

(15) Kou, L.; Frauenheim, T.; Chen, C. Nanoscale Multilayer Transition-Metal Dichalcogenide Heterostructures: Band Gap Modulation by Interfacial Strain and Spontaneous Polarization. J. Phys. Chem. Lett. 2013, 4, 1730–1736.

(16) Conley, H. J.; Wang, B.; Ziegler, J. I.; Haglund, R. F.; Pantelides, S. T.; Bolotin, K. I. Bandgap engineering of strained monolayer and bilayer MoS₂, Nano Lett. 2013, 13, 3626–3630.

(17) Su, X.; Ju, W.; Zhang, R.; Guo, C.; Zheng, J.; Yong, Y.; Li, X. Bandgap engineering of MoS₂/MX₂ (MX₂ = WS₂, MoSe₂ and WSe₂) heterobilayers subjected to biaxial strain and normal compressive strain. RSC Adv. 2016, 6, 18319–18325.

(18) Li, T.; Galli, G. Electronic properties of MoS₂ nanoparticles. J. Phys. Chem. C 2007, 111, 16192–16196.

(19) Splendiani, A.; Sun, L.; Zhang, Y.; Li, T.; Kim, J.; Chim, C.-Y.; Galli, G.; Wang, F. Emerging photoluminescence in monolayer MoS₂. Nano Lett. 2010, 10, 1271–1275.

(20) Ellis, J. K.; Lucero, M. J.; Scuseria, G. E. The indirect to direct transition in the indirect bandgap of silicon. Sci. Bull. 2016, 63, 1860–1864.

(21) Auteis, G.; Isaea, A.; Moreshchini, L.; Johannsen, J. C.; Pisoni, A.; Mori, R.; Zhang, W.; Filatova, T. G.; Kuznetsov, A. N.; Forro, L.; Van Den Broek, W.; Kim, Y.; Kim, K. S.; Lanzara, A.; Denlinger, J. D.; Rotenberg, E.; Bostwick, A.; Grioni, M.; Yazyev, O. V. A novel quasi-one-dimensional topological insulator in bismuth iodide β-Bi₂I₃. Nat. Mater. 2016, 15, 154–158.

(22) Suh, J.; Tan, T. L.; Zhao, W.; Park, J.; Lin, D.-Y.; Park, T.-E.; Xia, Z.; Fang, H.; Zhang, X.; Molokeev, M. S.; Gautier, R.; Yan, J.; Yang, J.; Xu, D. Thermoelectric characterization of individual bismuth selenide topological insulator nanoribbons. Nano Scale 2015, 7, 6683–6690.

(23) Wu, C.-I.; Li, L.-J.; Chen, L.-J.; He, J.-H. Superconductivity in Ultrathin NbSe2 Layers. Phys. Rev. B: Condens. Matter Mater. Phys. 2013, 87, 132508.

(24) Zhu, Y.; Zhu, H.; Soukoulis, C. M. 1D SbSeI, SbSI, and SbSBr With a New Thermoelectric Material: CsBi₄Te₆. Science 2000, 287, 1024–1027.

(25) Peng, B.; Xu, X.; Zhang, H.; Ning, Z.; Shao, H.; Ni, G.; Li, J.; Zhu, Y.; Zhu, H.; Soukoulis, C. M. 1D SbSe/SbS and SbBr With High Stability and Novel Properties for Microelectronic, Optoelectronic, and Thermoelectric Applications. Adv. Theory Simul. 2018, 1, 1700005.

(26) Island, J. O.; Barawi, M.; Biele, R.; Almagaz, A.; Clamagirand, J. M.; Ares, J. R.; Sánchez, C.; Van Der Zant, H. S. J.; Alvarez, J. V.; D’Agosta, R.; Ferrer, I. J.; Castellanos-Gomez, A.; Xu, D. Thermoelectric characterization of individual bismuth selenide topological insulator nanoribbons. ACS Nano 2018, 12, 7253–7263.

(27) Wang, Y.; Liu, Z.; Wang, C.; Yi, X.; Chen, R.; Ma, L.; Hu, Y.; Zhu, G.; Chen, T.; Tie, Z.; Ma, J.; Liu, J.; Jin, Z. Highly Branched VS₃ Nanodendrites with 1D Atomic-Chain Structure as a Promising Cathode Material for Long-Cycling Magnesium Batteries. Adv. Mater. 2018, 30, 1802563.

(28) Zhou, Y.; Wang, L.; Chen, S.; Qin, S.; Liu, X.; Chen, J.; Xue, D.-J.; Luo, M.; Cao, Y.; Cheng, Y.; Sargent, E. H.; Tang, J.; Thin-film SbSe, photovoltaics with oriented one-dimensional ribbons and benign grain boundaries. Nat. Photonics 2015, 9, 409–415.

(29) Wang, L.; Li, D.-B.; Li, K.; Chen, C.; Deng, H.-X.; Gao, L.; Zhao, Y.; Jiang, F.; Li, L.; Huang, F. Stable 6%-efficient Sb₂Se₃ solar cells with a ZnO buffer layer. ACS Nano 2018, 12, 27046.

(30) Yang, W.; Ahn, J.; Oh, Y.; Tan, J.; Lee, H.; Park, J.; Kwon, H.-C.; Kim, J.; Jo, W.; Kim, J.; Moon, J. Adjusting the Anisotropy of 1D Bandgap Insulator transition in quasi-one-dimensional single-crystal Nb₃Pd₃S₅ nanowires. Nano Lett. 2015, 15, 869–875.

(31) Zvybtsev, S. G.; Pokrovskii, V. Y.; Nasretdinova, V. F.; Zaitsev-Zotov, S. V.; Pavlovskiy, V. V.; Odobasco, A. B.; Pai, W. W.; Chu, M. W.; Lin, Y. G.; Zupanić, E.; Van Middelen, H. J. P.; Šturm, S.; Tchernychova, E.; Prodan, A.; Bennett, J. C.; Mukhamedshin, I. R.; Chernysheva, O. V.; Menušenkov, A. P.; Loginov, V. B.; Loginov, B. A.; Titov, A. N.; Abdel-Hafiez, M. NbS₂: A unique quasi-one-dimensional topological insulator with three charge density wave transitions. Phys. Rev. B 2017, 95, 035110.
(44) Stolyarov, M. A.; Liu, G.; Bloodgood, M. A.; Aytan, E.; Jiang, C.; Sannakay, R.; Salguero, T. T.; Nika, D. L.; Rumyantsev, S. L.; Shur, M. S.; Bozhilov, K. N.; Balandin, A. A. Breakdown current density in: H-BN-capped quasi-1D TaSe₃ metallic nanowires: Prospects of interconnect applications. Nanoscale 2016, 8, 15774–15782.

(45) Furuseth, S.; Brattås, L.; Kjekshus, A.; Andresen, A. F.; Fischer, P. On the Crystal Structures of Ti₃S₂, ZrS₂, ZrSe₂, ZrTe₃, HSn₃, and HSe₃. Acta Chem. Scand. 1975, 29a, 623–631.

(46) Island, J. O.; Molina-Mendoza, A. J.; Barawi, M.; Biele, R.; Flores, E.; Clamagirand, J. M.; Ares, J. R.; Sánchez, C.; van der Zant, H. S. J.; D’Agosta, R.; Ferrer, I. J.; Castellanos-Gomez, A. Electronics and optoelectronics of quasi-1D layered transition metal trichalcogenides. 2D Mater 2015, 4, 022003.

(47) Srivastava, S. K.; Avasthi, B. N. Preparation, structure and properties of transition metal trichalcogenides. J. Mater. Sci. 1992, 27, 3693–3705.

(48) Geremew, A.; Bloodgood, M. A.; Aytan, E.; Woo, B. W. K.; Corber, S. R.; Liu, G.; Bozhilov, K.; Salguero, T. T.; Rumyantsev, S.; Rao, M. P.; Balandin, A. A. Current Carrying Capacity of Quasi-1D ZrTe₃ Van Der Waals Nanoribbons. IEEE Electron Device Lett. 2018, 39, 735–738.

(49) Geremew, A. K.; Rumyantsev, S.; Bloodgood, M. A.; Salguero, T. T.; Balandin, A. A. Unique features of the generation-recombination noise in quasi-one-dimensional van der Waals nanoribbons. Nanoscale 2018, 10, 19749–19756.

(50) Empante, T. A.; Martinez, A.; Wurch, M.; Zhu, Y.; Geremew, A. K.; Yamaguchi, K.; Isarraraz, M.; Rumyantsev, S.; Reed, E. J.; Balandin, A. A.; Bartels, L. Low Resistivity and High Breakdown Current Density of 10 nm Diameter van der Waals TaSe₃ Nanowires by Chemical Vapor Deposition. Nano Lett. 2019, 19, 4355–4361.

(51) Meerschaut, A.; Guémas, L.; Berger, R.; Rouxel, J. The crystal structure of niobium selenide Nb₂Se₉ from twin-crystal data. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 1979, 35, 1747–1750.

(52) Rouxel, J. Synthesis and properties of low-dimensional metal chalcogenides. J. Solid State Chem. 1986, 64, 305–321.

(53) Sanjínès, R.; Berger, H.; Lévy, F. Synthesis and characterization of Nb₂Se₉ single crystals grown in molten solution. Mater. Res. Bull. 1988, 23, 549–553.

(54) Furuseth, S.; Klewe, B.; Pedersen, E.; Petersen, A.; Ohtaki, H. Crystal Structure and Properties of V₂Se₅. Acta Chem. Scand. 1984, 38a, 467–471.

(55) Oh, S.; Chae, S.; Kim, B. J.; Choi, K. H.; Jang, W.-S.; Jang, J.; Hussain, Y.; Lee, D. K.; Kim, Y.-M.; Yu, H. K.; Choi, J.-Y. Synthesis of a one-dimensional atomic crystal of vanadium selenide (V₂Se₅). RSC Adv. 2018, 8, 33980–33984.

(56) Oh, S.; Chae, S.; Kim, B. J.; Siddiqi, A. J.; Choi, K. H.; Jang, W. S.; Lee, K. H.; Kim, H. Y.; Lee, D. K.; Kim, Y. M.; Yu, H. K.; Choi, J. Y. Inorganic Molecular Chain Nb₂Se₉: Synthesis of Bulk Crystal and One-Atom-Thick Level Exfoliation. Phys. Status Solidi RRL 2018, 12, 1800401.

(57) Chae, S.; Siddiqi, A.; Oh, S.; Kim, C.; Choi, K. J.; Jang, W.-S.; Kim, Y.-M.; Yu, H.; Choi, J.-Y. Isolation of Nb₂Se₉ Molecular Chain from Bulk One-Dimensional Crystal by Liquid Exfoliation. Nanomaterials 2018, 8, 794.

(58) Chae, S.; Siddiqi, A. J.; Kim, B. J.; Oh, S.; Choi, K. H.; Lee, K. H.; Kim, H. Y.; Yu, H. K.; Choi, J.-Y. Isolation of inorganic molecular chains from rod-like bulk V₂Se₅ crystal by liquid exfoliation. RSC Adv. 2018, 8, 35348–35352.

(59) Lee, W.-G.; Chae, S.; Chung, Y. K.; Oh, S.; Choi, J.-Y.; Huh, J. New One-Dimensional Material Nb₂Se₉: Theoretical Prediction of Indirect to Direct Band Gap Transition due to Dimensional Reduction. Phys. Status Solidi RRL 2019, 13, 1800517.

(60) Lee, W.-G.; Chae, S.; Chung, Y. K.; Yoon, W.-S.; Choi, J.-Y.; Huh, J. Indirect-To-Direct Band Gap Transition of One-Dimensional V₂Se₅: Theoretical Study with Dispersion Energy Correction. ACS Omega 2019, 4, 18392–18397.