Semiconductor-to-metal transition in bilayer MoSi$_2$N$_4$ and WSi$_2$N$_4$ with strain and electric field

Cite as: Appl. Phys. Lett. 118, 113102 (2021); https://doi.org/10.1063/5.0044431
Submitted: 16 January 2021. Accepted: 06 February 2021. Published Online: 16 March 2021

Qingyun Wu, Liemao Cao, Yee Sin Ang, and Lay Kee Ang

COLLECTIONS

This paper was selected as Featured
This paper was selected as Scilight

Challenge us.
What are your needs for periodic signal detection? Watch

© 2021 Author(s).
Semiconductor-to-metal transition in bilayer MoSi$_2$N$_4$ and WSi$_2$N$_4$ with strain and electric field

Qingyun Wu,$^{1,3}$a) Liemao Cao,$^2$ Yee Sin Ang,$^1,a)$ and Lay Kee Ang$^{1,a)$

AFFILIATIONS

$^1$Science, Mathematics, and Technology, Singapore University of Technology and Design (SUTD), 8 Somapah Road, Singapore 487372, Singapore

$^2$College of Physics and Electronic Engineering, Hengyang Normal University, Hengyang 421002, China

a)Authors to whom correspondence should be addressed: qingyun_wu@sutd.edu.sg and ricky_ang@sutd.edu.sg

ABSTRACT

With exceptional electrical and mechanical properties and at the same time air-stability, layered MoSi$_2$N$_4$ has recently drawn great attention. However, band structure engineering via strain and electric field, which is vital for practical applications, has not yet been explored. In this work, we show that the biaxial strain and external electric field are effective ways for the bandgap engineering of bilayer MoSi$_2$N$_4$ and WSi$_2$N$_4$. It is found that strain can lead to indirect bandgap to direct bandgap transition. On the other hand, electric field can result in semiconductor to metal transition. Our study provides insights into the band structure engineering of bilayer MoSi$_2$N$_4$ and WSi$_2$N$_4$ and would pave the way for its future nanoelectronics and optoelectronics applications.

Published under license by AIP Publishing. https://doi.org/10.1063/5.0044431
0.01 eV/Å. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof form (PBE)\(^4\) was chosen for the exchange-correlation functional in the calculations. The Heyd-Scuseria-Ernzerhof hybrid functional method (HSE)\(^5\) was also used to obtain the more accurate band structure of the bilayers. To take into account the weak van der Waals interactions in the bilayers, we adopted the DFT-D3 method with the Grimme scheme\(^6\)\(^,\)\(^7\) in the calculations. A 20 Å thick of vacuum layer was inserted between adjacent bilayers to eliminate the interactions from periodic images.\(^8\)

Based on our total energy calculations and also previous results,\(^3\) the AC stacking of the bilayer MoSi\(_2\)N\(_4\) and WSi\(_2\)N\(_4\) is the most stable bilayer configuration with the lowest total energy. Therefore, we only focus on the AC stacking in the following discussions. Figure 1(a) depicts the optimized geometric structure of the bilayer MoSi\(_2\)N\(_4\) and WSi\(_2\)N\(_4\). Our calculated lattice parameter of the bilayer MoSi\(_2\)N\(_4\) and WSi\(_2\)N\(_4\) is \(a = 2.90 / 2.90\) Å, which is in good agreement with previous calculated results.\(^9\) As shown in Fig. 1(b), the band structure of the bilayer MoSi\(_2\)N\(_4\) and WSi\(_2\)N\(_4\) is very similar to its monolayer counterpart with only small splitting in energy bands induced by the interlayer interactions, which slightly reduces the bandgap. The indirect bandgap of the bilayer MoSi\(_2\)N\(_4\) and WSi\(_2\)N\(_4\) is calculated to be 1.64/1.94 eV. To obtain a more accurate band structure, the HSE hybrid functional calculations were also performed. It is found that the shape of the HSE bands are similar to that of the PBE results with only valence bands
pushed down and conduction bands pushed up. We obtain the bandgap value of 2.22/2.56 eV for the bilayer MoSi$_2$N$_4$ and WSi$_2$N$_4$ in HSE calculations.

2D materials can sustain a relatively large amount of strain (15% - 30% for graphene, MoS$_2$, and phosphorene). It has been proved that strain engineering is an effective avenue to modulate the electric, magnetic, and optical properties of 2D layered materials. To understand the tunability of the energy bandgap of the bilayer MoSi$_2$N$_4$ and WSi$_2$N$_4$, we applied biaxial strain to the system. The strain ($\varepsilon$) is evaluated using $\varepsilon = (a - a_0)/a_0 \times 100\%$, where $a$ and $a_0$ are the lattice parameter of the strained and unstrained bilayer, respectively. Figure 2(a) shows the evolution of the bandgap as a function of applied strain for bilayer MoSi$_2$N$_4$ and WSi$_2$N$_4$. It is suggested that the bandgap undergoes a monotonous decreasing with the increasing tensile strain. However, with increasing compress strain, the bandgap increases then decreases at around -4% for the bilayer MoSi$_2$N$_4$ and -6% for the bilayer MoSi$_2$N$_4$. Besides varying the bandgap, more importantly, strain is also found to change an indirect bandgap semiconductor to a direct bandgap semiconductor at about -4% of compress strain for the bilayer MoSi$_2$N$_4$ (see supplementary material, Fig. S1). To understand the electronic structure engineering by strain, we draw the projected density of states (PDOS) and partial charge density corresponding to the valence band maximum (VBM) and conduction band minimum (CBM) for bilayer MoSi$_2$N$_4$ and WSi$_2$N$_4$ under -10% and 10% strain in Figs. 2(b) and 2(c). As can be seen from the figure, the VBM and CBM are mostly contributed from both the metal atoms of the top and bottom layer of the bilayer with an enlarged bandgap for the compress -10% strain in the PDOS. In the partial charge density plot, we see more $d_{xy}$ and $d_{x^2-y^2}$ orbitals for the metal atoms in VBM and CBM for the compress -10% strain. This is because the $d_{xy}$ and $d_{x^2-y^2}$ orbitals are favorable for the in-plane bonding. The reduced bond length of Mo/W-N under compress strain facilitates the in-plane bonding, as shown in Fig. 2(d). The VBM is mostly from the Mo/W atom of the bottom layer, and the CBM is mostly from the Mo/W atom of the top layer, respectively, with a reduced bandgap for the tensile 10% strain. This split of the VBM and CBM from the metal atoms of the two different layer can be understood from the shorten distance of two metal atoms, which increases the interlayer interactions as shown in Fig. 2(d). Different from the compressed case, we see more $d_{z^2}$ orbitals for the metal atoms in VBM and CBM for the tensile 10% strain. This is because the $d_{z^2}$ orbital is favorable for the out-of-plane bonding. When the bond length increases, the out-of-plane bonding becomes more significant and thus more $d_{z^2}$ orbitals.

Applying an external electric field perpendicular to the layered material is another effective way of tuning the properties of 2D layered materials. The evolution of the bandgap as a function of the applied electric field for bilayer MoSi$_2$N$_4$ and WSi$_2$N$_4$ is provided in Fig. 3(a). It is found that the bandgap decreases monotonously with the increasing electric field and closes at 6 V/nm for both bilayer MoSi$_2$N$_4$ and WSi$_2$N$_4$. It is also interesting to find that the CBM for MoSi$_2$N$_4$ is at...
the K point, while the CBM for WSi$_2$N$_4$ moves to the M point when the bandgap closes (see supplementary material, Fig. S2). To gain more insight to the electronic structure engineering by electric field, we plot the PDOS and partial charge density of VBM and CBM for bilayer MoSi$_2$N$_4$ and WSi$_2$N$_4$ under 0 V/nm and 5 V/nm electric field in Figs. 3(b) and 3(c). As can be seen from the figure, the overall shape of the PDOS of the bottom and top metal atoms almost remains the same under 5 V/nm electric field. However, the energy bands of the bottom metal atom shift up while the energy bands of the up atom shift down, which gradually closes the bandgap. Furthermore, the CBM of the bilayer WSi$_2$N$_4$ under 5 V/nm electric field comes from the top Si atom that can be observed both from the PDOS and the partial charge density plot. This explains why the CBM for WSi$_2$N$_4$ moves to the M point under 5 V/nm electric field. This bandgap engineering by external electric field can be interpreted from the charge redistribution of the bilayer MoSi$_2$N$_4$ and WSi$_2$N$_4$ under electric field as shown in Fig. 3(d). The charge density difference ($\Delta \rho$) is defined as $\Delta \rho = \rho_{E} - \rho_{0}$, where $\rho_{E}$ and $\rho_{0}$ are the charge densities of the bilayer MoSi$_2$N$_4$ and WSi$_2$N$_4$ with and without the external electric field, respectively. Here, positive (negative) $\Delta \rho$ indicates charge accumulation (depletion). As can be seen from the figure, there is charge accumulation in the bottom layer and depletion in the top layer. This leads to the VBM in the bottom layer shifting up and the CBM in the top layer shifting down, which reduces the energy bandgap.\textsuperscript{21} To check the results, we also performed DFT + U calculations. As PDOS under 6 V/nm electric field shown in supplementary material, Fig. S3, DFT + U results suggest the CBM of WSi$_2$N$_4$ is also from W atoms as in the case of MoSi$_2$N$_4$. Nevertheless, the trend of bandgap engineering by applied electric field retains. Due to the large Stark effect, which is the underlying physics of these phenomena, the critical electric field can be reduced by increasing the thickness of these materials.\textsuperscript{16,27}

In conclusion, we have shown that the biaxial strain and external electric field are effective ways for the bandgap engineering of bilayer MoSi$_2$N$_4$ and WSi$_2$N$_4$. Band gaps can be tuned by both compress and tensile strain. Compress strain can even lead to indirect bandgap transition. The change in Mo/W-N bond length and Mo-Mo/W-W distance induced by strain is the main reason for this band structure engineering. Electric field can also modulate the bandgap and even semiconductor to metal transition. Charge redistribution induced by the electric field accounts for the bandgap tuning. Our study suggests the strain and electric field tunable bilayer MoSi$_2$N$_4$ and WSi$_2$N$_4$ could be promising materials for the next generation nanoelectronics and optoelectronics.

See the supplementary material for the complete electronic band structures of bilayer MoSi$_2$N$_4$ and WSi$_2$N$_4$ under strain and external electric fields. Also PDOS under 6 V/nm external electric field without and with Hubbard U.

This work was supported by Singapore MOE Tier 2 (Grant No. 2018-T2-1-007). All the calculations were carried out using the computational resources provided by the National Supercomputing Centre (NUSCC) Singapore.

**DATA AVAILABILITY**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**REFERENCES**