Inducing Half-Metallicity in Monolayer MoSi$_2$N$_4$

Avijeet Ray, Shubham Tyagi, Nirpendra Singh,* and Udo Schwingenschlögl*  

Cite This: ACS Omega 2021, 6, 30371−30375

ABSTRACT: First-principles calculations are performed for the recently synthesized monolayer MoSi$_2$N$_4$ [Science 369, 670−674 (2020)]. We show that N vacancies are energetically favorable over Si vacancies, except for Fermi energies close to the conduction band edge in the N-rich environment, and induce half-metallicity. N and Si vacancies generate magnetic moments of 1.0 and 2.0 $\mu_B$, respectively, with potential applications in spintronics. We also demonstrate that N and Si vacancies can be used to effectively engineer the work function.

INTRODUCTION

The discovery of numerous 2D materials in the last decade revealed exciting physical phenomena and exotic properties,$^{1−6}$ and many of these materials now are in demand for industrial applications.$^7$ In this context, ref $^8$ achieved a breakthrough in the synthesis of monolayer MoSi$_2$N$_4$, representing a milestone in the development of ternary layered materials. In contrast to the direct band gap semiconductors [monolayer MoS$_2$ (1.89 eV) and WS$_2$ (2.05 eV)],$^9$ monolayer MoSi$_2$N$_4$ is an indirect band gap (1.74 eV) semiconductor with excellent stability in air under ambient conditions. The intrinsic electron ($\sim$270 cm$^2$ V$^{-1}$ s$^{-1}$) and hole ($\sim$1200 cm$^2$ V$^{-1}$ s$^{-1}$) mobilities at the K point of the Brillouin zone are 4−6 times higher than those of monolayer MoS$_2$. In addition, first-principles calculations point to the existence of a whole family of stable monolayers (MA$_2$Z$_4$, where M is an early transition metal, such as Mo, W, Ta, or Nb, A = Si or Ge, and Z = N, P, or As) with properties ranging from semiconductors to metals and from non-magnets to magnets, opening up uncharted territory for the device technology based on 2D materials. Immediately after the discovery of monolayer MoSi$_2$N$_4$ and its sister transition-metal nitrides, phosphides, and arsenides, the family gained great attention owing to a multitude of potential applications.$^{10−13}$

Recently, an intercalated architecture approach was employed to predict 66 family members that are both dynamically and thermodynamically stable.$^{14}$ In the present work, we address the initial and only synthesized family member, monolayer MoSi$_2$N$_4$, to clarify its defect properties. In particular, we focus on the magnetic behavior as ferromagnetic 2D materials are of great technological importance.$^{15−33}$ While monolayer MoSi$_2$N$_4$ is a non-magnetic semiconductor, we study how spin polarization can be introduced through defects.$^{34,35}$ We systematically investigate both N and Si vacancies, including their effect on the work function, which is a key parameter in device applications.$^{36,37}$

COMPUTATIONAL METHODS

Structural optimizations and calculations of the electronic properties of pristine and defective monolayer MoSi$_2$N$_4$ are performed using the projector augmented-wave method$^{38}$ of density functional theory, as implemented in the Vienna ab-initio simulation package.$^{39}$ We construct $3\times3\times1$ supercells of the monolayer MoSi$_2$N$_4$ unit cell to study vacancy defects. The lattice constants and atomic positions are optimized using the Perdew−Burke−Ernzerhof generalized gradient approximation until the total energy is converged to $10^{-6}$ eV, and the force on each atom is converged to 0.001 eV/Å. The electronic properties are evaluated by the Heyd−Scuseria−Ernzerhof hybrid functional.$^{40}$ We use a plane-wave cutoff energy of 500 eV, a $8\times8\times1$ k-mesh for the unit cell, and $4\times4\times1$ k-meshes for the supercells. We adopt the DFT-D3 method to account for the van der Waals interaction$^{41}$ and apply vacuum layers of 15 Å thickness to create 2D models. Spin−orbit coupling is not taken into account after checking that it has only minor effects on the electronic properties for the Perdew−Burke−Ernzerhof functional. Antiferromagnetic spin

Received: June 30, 2021
Accepted: October 22, 2021
Published: November 4, 2021
configurations are found to be unstable and converge to ferromagnetism.

**RESULTS AND DISCUSSION**

Monolayer MoSi₂N₄ has a hexagonal lattice with space group P6₃m1. The side view in Figure 1a illustrates that it is composed of covalently bonded MoN₂ and SiN layers, with a total thickness of 7.01 Å. The central MoN₂ layer resembles the structure of 2H−MoS₂, and the adjacent honeycomb SiN layers are slightly buckled. The stacking is such that the Mo atoms are located at the hollow sites of the Si₃N₃ hexagons, giving rise to Si−N interlayer bonds, see Figure 1a. We obtain for pristine monolayer MoSi₂N₄ an optimized lattice constant of 2.91 Å. The Si−N bond lengths in the out-of-plane and in-plane directions turn out to be 1.74 Å and 1.75 Å, respectively, the Mo−N bond length is 2.08 Å, the N−Si−N bond angles are 112 and 107°, and the N−Mo−N bond angles are 73 and 88°, in agreement with ref 8. It is important to notice that the structure has no inversion symmetry but a mirror plane in which the Mo atoms are located.

While we do not consider Mo vacancies due to their high formation energy, the crystal structures obtained in the presence of N_in, N_out, and Si vacancies are shown in Figure 1b–d. N_in and N_out label the N vacancies in the MoN₂ and SiN layers, respectively. The vacancy formation energy is calculated as

\[
E_i^{(q)} = E_{\text{vacancy}}^{(q)} - E_{\text{pristine}}^{(q)} + E_{\text{atom}}^{(q)} + qE_F + E_{\text{correction}}^{(q)}
\]

where \(E_{\text{vacancy}}^{(q)}\) is the total energy of monolayer MoSi₂N₄ with a vacancy of charge \(q\), \(E_{\text{pristine}}\) is the total energy of pristine monolayer MoSi₂N₄, \(E_{\text{atom}}\) is the total energy of the removed atom (obtained using the N₂ molecule or diamond silicon), \(E_F\) is the Fermi energy, and \(E_{\text{correction}}\) is evaluated by the Kumagai-Oba method using the Spinney package. The N_in, N_out, and Si vacancy formation energies are shown as functions of the Fermi energy in Figure 2a,b for the N-rich and Si-rich environment, respectively. Besides neutral vacancies, vacancy charges of −4 for Si and +3 for N are considered, in accordance with the oxidation numbers. We find for the N-rich environment that formation of N_out and Si vacancies is favorable below and above \(E_F = 1.38\) eV, respectively, and for the Si-rich environment that formation of N_out and N_in vacancies is favorable below and above \(E_F = 1.64\) eV.

The electron localization function is shown in Figure 3 for the (001) planes including the vacancies. High values between Si and N represent strong covalent bonding (compare Figure 1 for the crystal structure). Figure 3c points to enhanced environment, respectively.
modifications of the chemical bonding in the case of the Si vacancy, as compared to the \( N_{\text{in}} \) and \( N_{\text{out}} \) vacancies. The band structure of pristine monolayer MoSi\(_2\)N\(_4\) in Figure 4a shows an indirect band gap of 2.34 eV, while the experimental indirect band gap is 1.94 eV.\(^8\) The band structures in Figure 4b–d show that vacancies have a significant impact on the electronic states. Half-metallicity is induced by both the \( N_{\text{in}} \) and \( N_{\text{out}} \) vacancies as only spin-majority bands cross the Fermi energy, while the Si vacancy narrows the band gap to 0.58 eV. Notably, the N and Si vacancies generate magnetic moments of 1.0 and 2.0 \( \mu_B \), respectively, which is crucial for potential applications in spintronics. Low dispersions of the bands crossing the Fermi energy reflect heavy carriers in the case of the \( N_{\text{in}} \) vacancy, see Figure 4b.

The real-space spin-density distributions in Figure 5 indicate that the magnetic moment induced by the \( N_{\text{in}} \) vacancy is carried mainly by the adjacent Mo 4d orbitals. In the case of the \( N_{\text{out}} \) vacancy, it is carried by the adjacent Si 3p and N 2p orbitals with some contributions of the same orbitals at distant sites, and in the case of the Si vacancy, it is carried by the N 2p orbitals missing a Si bonding partner. Spin-polarized p orbitals are rather rare, while being attractive for spin injection and spin filtering due to the light carriers; see the substantial dispersions of the bands crossing the Fermi energy in Figure 4c.

As it is a key parameter for electronic devices, we evaluate the effects of the vacancies on the work function. We obtain for pristine monolayer MoSi\(_2\)N\(_4\) a work function of 5.28 eV, while the work functions of \( N_{\text{in}} \)-defective, \( N_{\text{out}} \)-defective, and Si-defective monolayer MoSi\(_2\)N\(_4\) turn out to be 4.75, 4.29, and
6.59 eV, respectively. Due to these large differences at moderate vacancy concentrations of 2.8% (N\textsubscript{in}-defective and N\textsubscript{out}-defective) and 5.6% (Si-defective), our results demonstrate that vacancies can be used to effectively engineer the work function by lowering it through N vacancies and enhancing it through Si vacancies according to the technological needs, particularly at interfaces.

**CONCLUSIONS**

We have calculated the formation energies of N and Si vacancies in monolayer MoSi\textsubscript{2}N\textsubscript{4}, finding that N vacancies are energetically favorable over Si vacancies except for Fermi energies close to the conduction band edge in the N-rich environment. Our results demonstrate that N vacancies induce half-metallicity. N and Si vacancies generate magnetic moments of 1.0 and 2.0 \( \mu_B \) respectively. As a consequence, applications in the field of spintronics are looming, for example, in spin injection and spin filtering due to the light carriers in the spin-polarized p orbitals. In particular, it turns out that the work function of monolayer MoSi\textsubscript{2}N\textsubscript{4} can be effectively adapted to the technological needs by controlling the (local) vacancy concentrations.

**AUTHOR INFORMATION**

**Corresponding Authors**

Udo Schwingenschlögl — Physical Science and Engineering Division (PSE), King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia; orcid.org/0000-0003-4179-7231; Email: udo.schwingenschlogl@kaust.edu.sa

Nirpendra Singh — Department of Physics and Center for Catalysis and Separation (CeCaS), Khalifa University of Science and Technology, Abu Dhabi 127788, United Arab Emirates; orcid.org/0000-0001-8043-0403; Email: nirpendra.singh@ku.ac.ae

**Authors**

Avijeet Ray — Physical Science and Engineering Division (PSE), King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

Shubham Tyagi — Physical Science and Engineering Division (PSE), King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c03444

**Notes**

The authors declare no competing financial interest.

The data that supports the findings of this study are available within the article.

**ACKNOWLEDGMENTS**

The research reported in this publication was supported by funding from King Abdullah University of Science and Technology (KAUST). The authors gratefully acknowledge the KAUST supercomputing laboratory for computational resources.

**REFERENCES**

(1) Naguib, M.; Kurtoglu, M.; Presser, V.; Lu, J.; Niu, J.; Heon, M.; Hultman, L.; Gogotsi, Y.; Barsoum, M. W. Two-dimensional nanocrystals produced by exfoliation of Ti\textsubscript{3}AlC\textsubscript{2}. *Adv. Mater.* 2011, 23, 4248–4253.

(2) Geim, A. K.; Grigorieva, I. V. Van der Waals heterostructures. *Nature* 2013, 499, 419–425.

(3) Naguib, M.; Mochalin, V. N.; Barsoum, M. W.; Gogotsi, Y. 25th anniversary article: MXenes: A new family of two-dimensional materials. *Adv. Mater.* 2014, 26, 992–1005.

(4) Toth, L. Transition metal carbides and nitrides; Elsevier: New York, 2014.

(5) Novoselov, K. S.; Mishchenko, A.; Carvalho, A.; Castro Neto, A. H. 2D materials and van der Waals heterostructures. *Science* 2016, 353, aac9439.

(6) Anasori, B.; Lukatskaya, M. R.; Gogotsi, Y. 2D metal carbides and nitrides (MXenes) for energy storage. *Nat. Rev. Mater.* 2017, 2, 16098.

(7) Geim, A. K.; Novoselov, K. S. Nanoscience and technology: A collection of reviews from nature journals; World Scientific: Singapore, 2010.

(8) Hong, Y.-L.; Liu, Z.; Wang, L.; Zhou, T.; Ma, W.; Xu, C.; Feng, S.; Chen, L.; Chen, M.-L.; Sun, D.-M.; Chen, X.-Q.; Cheng, H.-M.;
Ren, W. Chemical vapor deposition of layered two-dimensional MoSi2N2 materials. *Science* **2020**, *369*, 670–674.

(9) Kumar, A.; Ahluwalia, P. K. Electronic structure of transition metal dichalcogenides monolayers 1H-MX, (M = Mo, W; X = S, Se, Te) from ab-initio theory: New direct band gap semiconductors. *Eur. Phys. J. B* **2012**, *85*, 186.

(10) Li, S.; Wu, W.; Feng, X.; Guan, S.; Feng, W.; Yao, Y.; Yang, S. A. Valley-dependent properties of monolayer MoSi2N2, WSi2N2 and MoSi2As4. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2020**, *102*, 235435.

(11) Zhong, H.; Xiong, W.; Lv, P.; Yu, J.; Yuan, S. Strain-induced semiconductor to metal transition in MA3Z6 bilayers (M = Ti, Cr, Mo; A = Si; Z = N, P). *Phys. Rev. B: Condens. Matter Mater. Phys.* **2021**, *103*, 085124.

(12) Yang, C.; Song, Z.; Sun, X.; Lu, J. Valley pseudospin in monolayer MoSi2N2 and MoSi2As4. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2021**, *103*, 035308.

(13) Balekry, A.; Faraji, M.; Hoat, D. M.; Shahrokhi, M.; Fadlallah, M. M.; Shojaei, F.; Feghhi, S. A. H.; Ghergherehchi, M.; Gogova, D. MoSi2N2 single-layer: A novel two dimensional material with outstanding mechanical, thermal, electronic, optical, and photocatalytic properties. *J. Phys. D: Appl. Phys.* **2021**, *54*, 155303.

(14) Wang, L.; Shi, Y.; Liu, M.; Hong, Y. L.; Chen, M. X.; Li, R.; Gao, Q.; Ren, W.; Cheng, H. M.; Li, Y.; Chen, X. Q. Structure-driven intercalated architecture of septupleatom-layer MA3Z6 family with diverse properties from semiconductor to topological insulator to Ising superconductor. arXiv:2008.02981 **2020**.

(15) Friedland, K.-J.; Hey, R.; Kostial, H.; Klann, R.; Ploog, K. New concept for the reduction of impurity scattering in remotely doped GaAs quantum wells. *Phys. Rev. Lett.* **1996**, *77*, 4616–4619.

(16) Mak, K. F.; Lee, C.; Hone, J.; Shan, J.; Heinz, T. F. Atomically thin MoS2: A new direct-gap semiconductor. *Phys. Rev. Lett.* **2010**, *105*, 136805.

(17) Yoon, Y.; Ganapathi, K.; Salahuddin, S. How good can monolayer MoS2 transistors be? *Nano Lett.* **2011**, *11*, 3768–3773.

(18) Ataca, E.; Ciraci, S. Functionalization of single-layer MoS2 honeycomb structures. *J. Phys. Chem. C* **2011**, *115*, 13303–13311.

(19) Alam, K.; Lake, R. K. Monolayer MoS2 transistors beyond the technology road map. *IEEE Trans. Electron Devices* **2012**, *59*, 3250–3254.

(20) Ye, J. T.; Zhang, Y. J.; Akashi, R.; Bahramy, M. S.; Arita, R.; Iwasa, Y. Superconducting dome in a gate-tuned band insulator. *Science* **2012**, *338*, 1193–1196.

(21) Ma, Y.; Dai, Y.; Guo, M.; Niu, C.; Zhu, Y.; Huang, B. Evidence of the existence of magnetism in pristine VX2 monolayers (X = S, Se) and their strain-induced tunable magnetic properties. *ACS Nano* **2012**, *6*, 1695–1701.

(22) Zhou, Y.; Wang, Z.; Yang, P.; Xu, X.; Yang, L.; Sun, X.; Gao, F. Tensile strain switched ferromagnetism in layered NbSe2 and NbS2. *ACS Nano* **2012**, *6*, 9727–9736.

(23) Radisavljevic, B.; Kis, A. Mobility engineering and a metal-insulator transition in monolayer MoS2. *Nat. Mater.* **2013**, *12*, 815–820.

(24) Shi, H.; Pan, H.; Zhang, Y.-W.; Yakobson, B. I. Strong ferromagnetism in hydrogenated monolayer MoS2 tuned by strain. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2013**, *88*, 205305.

(25) Wu, S.; Ross, J. S.; Liu, G.-B.; Aivazian, G.; Jones, A.; Fei, Z.; Zhu, W.; Xiao, D.; Yao, W.; Cobden, D.; Xu, X. Electrical tuning of valley magnetic moment through symmetry control in bilayer MoS2. *Nat. Phys.* **2013**, *9*, 149–153.

(26) Rostami, H.; Moghadam, A. G.; Asgari, R. Effective lattice Hamiltonian for monolayer MoS2: Tailoring electronic structure with perpendicular electric and magnetic fields. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2013**, *88*, 085440.

(27) Jarirala, D.; Sangwan, V. K.; Lauhon, L. J.; Marks, T. J.; Hersam, M. C. Emerging device applications for semiconducting two-dimensional transition metal dichalcogenides. *ACS Nano* **2014**, *8*, 1102–1120.

(28) Pan, H. Magnetic and electronic evolutions of hydrogenated VTe2 monolayer under tension. *Sci. Rep.* **2014**, *4*, 7524.

(29) Pan, H. Electronic and magnetic properties of vanadium dichalcogenides monolayers tuned by hydrogenation. *J. Phys. Chem. C* **2014**, *118*, 13248–13253.

(30) Loh, G. C.; Pandey, R. Robust magnetic domains in fluorinated ReMo2Te3 monolayer. *Phys. Chem. Chem. Phys.* **2015**, *17*, 18843–18853.

(31) Xi, X.; Zhao, L.; Wang, Z.; Berger, H.; Forró, L.; Shan, J.; Mak, K. F. Strongly enhanced charge-density-wave order in monolayer NbSe2. *Nat. Nanotechnol.* **2015**, *10*, 765–769.

(32) Manchanda, P.; Sharma, V.; Yu, H.; Sellmyer, D. J.; Skomski, R. Magnetism of Ta dichalcogenide monolayers tuned by strain and hydrothermal. *Appl. Phys. Lett.* **2015**, *107*, 032402.

(33) Manchanda, P.; Skomski, R. 2D transition-metal diselenides: Phase segregation, electronic structure, and magnetism. *J. Phys. Condens. Matter* **2016**, *28*, 064002.

(34) Cai, L.; He, J.; Liu, Q.; Yao, T.; Chen, L.; Yan, W.; Hu, F.; Jiang, Y.; Zhao, Y.; Hu, T.; Sun, Z.; Wei, S. Vacancy-induced ferromagnetism of MoS2 nanosheets. *J. Am. Chem. Soc.* **2015**, *137*, 2622–2627.

(35) Lin, Z.; Carvalho, B. R.; Kahn, E.; Lv, R.; Rao, R.; Terrones, H.; Pimenta, M. A.; Terrones, M. Defect engineering of two-dimensional transition metal dichalcogenides. *2D Mater.* **2016**, *3*, 022002.

(36) Ma, Y.; Shen, C.; Zhang, A.; Chen, L.; Liu, Y.; Chen, J.; Liu, Q.; Li, Z.; Amer, M. R.; Nilges, T.; Abbas, A. M.; Zhou, C. Black phosphorus field-effect transistors with work function tunable contacts. *ACS Nano* **2017**, *11*, 7126–7133.

(37) Baik, S. S.; Im, S.; Choi, H. J. Work function tuning in two-dimensional MoS2 field-effect-transistors with graphene and graphene source-drain contacts. *Sci. Rep.* **2017**, *7*, 45546.

(38) Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1994**, *501*, 17953–17979.

(39) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented wave method. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1999**, *59*, 17858–17875.

(40) Heyd, J.; Scuseria, G. E.; Ernzerhof, M. Hybrid functionals based on a screened Coulomb potential. *J. Chem. Phys.* **2003**, *118*, 8207–8215.

(41) Grimmer, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104.

(42) Guo, Y.; Liu, D.; Robertson, J. Chalcogen vacancies in monolayer transition metal dichalcogenides and Fermi level pinning at contacts. *Appl. Phys. Lett.* **2015**, *106*, 173106.

(43) Zhang, S. B.; Northrup, J. E. Chemical potential dependence of defect formation energies in GaAs: Application to Ga self-diffusion. *Phys. Rev. Lett.* **1991**, *67*, 2339–2342.

(44) Kamagai, Y.; Oba, F. Electrostatics-based finite-size corrections for first-principles point defect calculations. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1991**, *89*, 195205.

(45) Arrigoni, Marco; Madsen, Georg K.H. Spinney: Post-processing of first-principles calculations of point defects in semiconductors with Python. *Comput. Phys. Commun.* **2021**, *264*, 107946.