Predicted septuple-atomic-layer Janus MSiGeN$_4$ (M=Mo and W) monolayers with Rashba spin splitting and high electron carrier mobilities

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Janus two-dimensional (2D) materials have attracted much attention due to possessing unique properties caused by their out-of-plane asymmetry, which have been achieved in many 2D families. In this work, the Janus monolayers are predicted in new 2D MA$_i$Z$_4$ family by means of first-principles calculations, MoSi$_2$N$_4$ and WSi$_2$N$_4$ of which have been synthesized in experiment (Science 369, 670-674 (2020)). The predicted MSiGeN$_4$ (M=Mo and W) monolayers exhibit dynamic, thermodynamical and mechanical stability, and they are indirect band-gap semiconductors. The inclusion of spin-orbit coupling (SOC) gives rise to the Rashba-type spin splitting, which is observed in the valence bands, being different from common conduction bands. Calculated results show valley polarization at the edge of the conduction bands due to SOC together with inversion symmetry breaking. It is found that MSiGeN$_4$ (M=Mo and W) monolayers have high electron mobilities. Both in-plane and much weak out-of-plane piezoelectric polarizations can be observed, when a uniaxial strain in the basal plane is applied. The values of piezoelectric strain coefficient $d_{11}$ of the Janus MSiGeN$_4$ (M=Mo and W) monolayers fall between those of the MSi$_2$N$_4$ (M=Mo and W) and MGe$_2$N$_4$ (M=Mo and W) monolayers, as expected. It is proved that strain can tune the positions of valence band maximum (VBM) and conduction band minimum (CBM), and enhance the the strength of conduction bands convergence caused by compressive strain. It is also found that tensile biaxial strain can enhance $d_{11}$ of MSiGeN$_4$ (M=Mo and W) monolayers, and the compressive strain can improve the $d_{11}$ (absolute values). Our predicted MSiGeN$_4$ (M=Mo and W) monolayers as derivatives of 2D MA$_i$Z$_4$ family enrich Janus 2D materials, and can motivate related experimental works.

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I. INTRODUCTION

The exploration of graphene$^1$ enormously promotes the search for new 2D materials both in experiment and in theory, which have potential applications in the field of optoelectronics, spintronics, valleytronics and energy conversion and storage. Numerous 2D materials have been found, including transition metal chalcogenides (TMDs), group-VA, group-IV-VI, group-IV, transition metal carbides/nitrides (MXenes), Cr$_2$Ge$_2$Te$_6$, Mn$_2$C$_6$Se$_{12}$ and Mn$_2$C$_6$S$_6$Se$_6$ monolayers$^{2,13}$. The unique crystal structure together with strong SOC in monolayer TMDs demonstrates coupled spin-valley physics$^{14}$, and the buckled honeycomb structure plus strong SOC can give rise to quantum spin Hall (QSH) and quantum anomalous Hall (QAH) effects in a particular type of 2D Xene$^{15,16}$. An emerging class of 2D materials (Janus 2D materials) have currently attracted increasing attention due to unique crystal structures, which lack the reflection symmetry with respect to the central atomic layer$^{17}$. In these 2D Janus materials, the strong Rashba spin splitting, second harmonic generation response and out-of-plane piezoelectric polarizations can be achieved$^{17}$. Many Janus 2D materials have been proposed, such as Janus graphene, asymmetrically functionalizing silicene monolayer, Janus TMDs, Janus transition-metal oxides, PtSSe, TiXY (X/Y=S, Se and Te), VSSe, SnSSe and Janus group-III monochalcogenide M$_2$XY (M=Ga, In, X/Y=S, Se, Te)$^{18-26}$. Recently, Janus monolayer MoSe$_2$ has been successfully achieved by different experimental strategies$^{27}$ with additional out-of-plane piezoelectric coefficient$^{28,29}$.

Recently, by chemical vapor deposition (CVD), the septuple-atomic-layer 2D MoSi$_2$N$_4$ and WSi$_2$N$_4$ have been synthesized$^{30}$, which opens up a new 2D material family. The density functional theory (DFT) calculations predict many similar 2D materials with a general formula of MA$_i$Z$_4$, where M represents an early transition metal (W, V, Nb, Ta, Ti, Zr, Hf, or Cr), A is Si or Ge, and Z stands for N, P, or As$^{30}$. In quick succession, by intercalating MoS$_2$-type MZ$_2$ monolayer into InSe-type A$_2$Z$_2$ monolayer, twelve kinds of 2D family MA$_i$Z$_4$ are proposed with $\alpha_i$ and $\beta_i$ ($i=1$ to 6) phases with diverse properties from semiconductor to topological insulator to Ising superconductor$^{31}$. Intrinsic piezoelectricity in monolayer MSi$_2$N$_4$ (M=Mo, W, Cr, Ti, Zr and Hf) has been predicted by the first-principle calculations$^{32}$. It is also predicted that the strain can effectively tune the electronic properties of VS$_2$P$_4$ monolayer, and it undergoes ferromagnetic metal (FMM) to spin-gapless semi-
FIG. 1. (Color online) The top view (a) and side view (b) crystal structure of MSiGeN$_4$ (M=Mo and W) monolayer. The rhombus primitive cell and the rectangle supercell are marked by black and green lines.

FIG. 2. (Color online) The phonon band dispersions of MSiGeN$_4$ (M=Mo and W).

TABLE I. For MSiGeN$_4$ (M=Mo and W) monolayers, the lattice constants $a_0$ (Å), the gaps with GGA and GGA+SOC (eV), and Rashba energy (meV).

| Name       | $a_0$  | Gap    | Gap-SOC | $E_R$ |
|------------|--------|--------|---------|-------|
| MoSiGeN$_4$ | 2.963  | 1.116  | 1.126   | 0.8   |
| WSiGeN$_4$ | 2.964  | 1.428  | 1.408   | 4.2   |

It’s a natural idea to achieve Janus 2D materials in the new septuple-atomic-layer 2D MA$_2$Z$_4$ family. In this work, inspiring from the already synthesized MSi$_2$N$_4$ (M=Mo and W) by introducing Si during CVD growth of M$_2$N (M=Mo and W) $^{30}$, we construct the MSiGeN$_4$ (M=Mo and W) monolayers, which may be achieved by introducing Si and Ge during CVD growth of M$_2$N (M=Mo and W). Their electronic structures, carrier mobilities and piezoelectric properties have been investigated, and show distinct Rashba spin splitting and out-of-plane piezoelectric polarizations compared to MSi$_2$N$_4$ (M=Mo and W) monolayers $^{32}$. It is found that the strain can effectively tune the electronic structures and piezoelectric properties of MSiGeN$_4$ (M=Mo and W) monolayers, along with strain effects on their electronic structures and piezoelectric properties. Finally, we shall give our discussion and conclusions.

II. COMPUTATIONAL DETAIL

We perform DFT$^{36}$ calculations for structural relaxation and electronic structures by using the Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) for the exchange and correlation function, as implemented in the Vienna ab initio simulation package (VASP)$^{37-40}$. To describe the electron-ion interaction, we use the projector augmented wave (PAW) method. For energy band calculations of MSiGeN$_4$ (M=Mo and W) monolayers, the SOC is also taken into account. A cutoff energy of 500 eV for the plane wave basis set is used to ensure an accurate DFT calculations. For the convergence of electronic self-consistent calculations, the total energy convergence criterion is set to $10^{-8}$ eV, and the Hellmann-Feynman forces on each atom are less than 0.0001 eV Å$^{-1}$. A vacuum spacing of more than 32 Å is adopted to decouple the spurious interaction between the layers.

The coefficients of the elastic stiffness tensor $C_{ij}$ and piezoelectric stress coefficients $e_{ij}$ are calculated by using strain-stress relationship (SSR) and density functional perturbation theory (DFPT) method$^{41}$, respectively. The Brillouin zone sampling is done using a Monkhorst-Pack mesh of $16 \times 16 \times 1$ for $C_{ij}$, and $9 \times 16 \times 1$ for $e_{ij}$. The 2D elastic coefficients $C_{ij}^{2D}$ and piezoelectric stress coefficients $e_{ij}^{2D}$ have been renormalized by the
III. STRUCTURE AND STABILITY

The top view and side view of crystal structure of MSiGeN$_4$ (M=Mo and W) monolayers are shown in Figure 1, and the rhombohedral unit cell and the rectangle supercell are shown. The structure of monolayer MSiGeN$_4$ (M=Mo and W) could be regarded as a MN$_2$ layer sandwiched by Si-N and Ge-N bilayers, which can be constructed by replacing the Si/Ge atoms of top SiN/GeN bilayer in MSi$_2$N$_4$/MG$_2$N$_4$ monolayer with Ge/N atoms. If the Si-N or Ge-N bilayers is considered as a whole, the MSiGeN$_4$ (M=Mo and W) monolayers can be viewed as Janus 2D materials. The symmetry of MSiGeN$_4$ (M=Mo and W) monolayers (No. 156) is lower than that of the MSi$_2$N$_4$/MG$_2$N$_4$ monolayer (No. 187) due to the lack of the reflection symmetry with respect to the central M atomic layer. The reduced symmetry can lead to many novel properties, such as Rashba spin splitting and out-of-plane piezoelectric polarizations.

The optimized lattice constants of MoSiGeN$_4$/WSiGeN$_4$ is $a=b=2.963/2.964$ Å with GGA, being between the ones of MoSi$_2$N$_4$ (2.91 Å)/WSi$_2$N$_4$ (2.91 Å) and MoGe$_2$N$_4$ (3.02 Å)/WG$_2$N$_4$ (3.02 Å). The dynamical stability of the MSiGeN$_4$ (M=Mo and W) monolayers are tested by analyzing the phonon spectra. Their phonon band dispersions calculated along the high-symmetry directions of the Brillouin zone are shown in Figure 2. The 18 optical and 3 acoustical phonon branches as a total of 21 branches due to 7 atoms per cell are observed. It is clearly seen that the outlines of phonon band dispersions between MoSiGeN$_4$ and WSiGeN$_4$ are very similar. It is noted that the out-of-plane acoustic (ZA) branch corresponding to the out-of-plane vibrations deviates from linearity, which agrees well with the conclusion that the ZA phonon branch should have quadratic dispersion, when the sheet is free of stress. All phonon frequencies of the MSiGeN$_4$ (M=Mo and W) monolayers are positive, which confirms their dynamical stability, and they can exist as free-standing 2D materials.

It is important to check the mechanical stability of the MSiGeN$_4$ (M=Mo and W) monolayers by elastic constants $C_{ij}$. The hexagonal symmetry leads to two independent elastic constants $C_{11}$ and $C_{12}$ for MSiGeN$_4$ (M=Mo and W) monolayers. The calculated $C_{11}=C_{22}=486.71$ Nm$^{-1}$/508.27 Nm$^{-1}$ and $C_{12}=144.14$ Nm$^{-1}$/147.21 Nm$^{-1}$ for MoSiGeN$_4$/WSiGeN$_4$ monolayer. For hexagonal symmetry, the mechanical stability of a material should satisfy the Born criteria of mechanical stability:

$$C_{11} > 0, \quad C_{66} > 0$$

where the $C_{66}=C_{11}-C_{12}/2$. The calculated $C_{ij}$ confirm the mechanical stability of MSiGeN$_4$ (M=Mo and W) monolayers. The Young’s modulus $C_{2D}(\theta)$ can be calculated on the basis of the elastic constants:

$$C_{2D}(\theta) = \frac{C_{11}C_{22} - C_{12}^2}{C_{11}\sin^2\theta + Asin^2\theta\cos^2\theta + C_{22}\cos^2\theta}$$
where $A = (C_{11}C_{22} - C_{12}^2)/C_{66} - 2C_{12}$. It is worth noting that MSiGeN$_4$ (M=Mo and W) monolayers are mechanically isotropic. The calculated $C_{2D}$ is 444.02 Nm$^{-1}$/465.63 Nm$^{-1}$ for MoSiGeN$_4$/WSiGeN$_4$ monolayer, which are larger than ones of most 2D materials$^{48-51}$, indicating that these monolayers are rigid. The Poisson’s ratio $\nu(\theta)$ is also isotropic, and can be attained by:

$$\nu^{2D} = \frac{C_{12}}{C_{11}}$$  \hspace{1cm} (3)

The calculated $\nu$ is 0.296/0.290 for MoSiGeN$_4$/WSiGeN$_4$ monolayer.

To verify the stability of the MSiGeN$_4$ (M=Mo and W) monolayers at room temperature, ab initio molecular dynamics (AIMD) simulations are carried out with a supercell of size $4 \times 4 \times 1$ for more than 3000 fs with a time step of 1 fs. The total energy fluctuations of MSiGeN$_4$ (M=Mo and W) monolayers as a function of simulation time together with crystal structures at 300 K after the simulation for 3 ps are shown in FIG.1 of ESI. Calculated results show no obvious structural disruption with the total energy fluctuates being small after 3 ps at 300 K, which proves that MSiGeN$_4$ (M=Mo and W) monolayers are thermodynamically stable.

The dynamical, thermal and mechanical stability of the MSiGeN$_4$ (M=Mo and W) monolayers are proved by phonon calculations, AIMD and elastic constants, suggesting the possible synthesis of these monolayers. By introducing Si during CVD growth of M$_2$N (M=Mo and W), monolayer MSi$_2$N$_4$ (M=Mo and W) have been synthesized in experiment$^{30}$. If the Si and Ge are simultaneously introduced during CVD growth of M$_2$N (M=Mo and W) to passivate its surface, it is possible to achieve MSiGeN$_4$ (M=Mo and W) monolayers.

IV. ELECTRONIC STRUCTURE

Due to containing transition metal in MSiGeN$_4$ (M=Mo and W) monolayers, the SOC is also taken into account. In fact, it has been proved that the SOC has important effects on electronic structures of monolayer MSi$_2$N$_4$ (M=Mo and W), which exhibit rich spin-valley physics$^{31,34,35}$. Therefore, the SOC is considered for electronic structure calculations of MSiGeN$_4$ (M=Mo and W) monolayers, and their energy band structures with both GGA and GGA+SOC are plotted in Figure 3. Both GGA and GGA+SOC results show that MSiGeN$_4$ (M=Mo and W) monolayers are indirect gap semiconductors with the CBM at K point. To accurately determine VBM, the enlarged views of the valence bands near the Fermi level for MSiGeN$_4$ (M=Mo and W) monolayers using GGA and GGA+SOC are plotted in Figure 4. For GGA results, the valence bands of MoSiGeN$_4$ around the $\Gamma$ point near the Fermi level are flat with the error less than 1 meV, and the VBM of WSiGeN$_4$ deviates slightly from the $\Gamma$ point. Due to the intrinsic out-of-plane electric field induced by the mirror asymmetry, the Rashba-type spin splitting around the $\Gamma$ point is observed, when the SOC is included. This gives rise to the deviation of VBM of MSiGeN$_4$ (M=Mo and W) monolayers with GGA+SOC.
It is found that the gap values of MSiGeN\textsubscript{4} (M=Mo and W) monolayers between GGA and GGA+SOC are very close, and the related data are summarized in Table I.

From FIG.2 of ESI, the Zeeman-type spin splitting around K/K1 point (the degenerate K and K1 valleys ) in the valence bands near the Fermi level is observed due to SOC together with inversion symmetry breaking. The respective time-reversal symmetry requires that the spin splitting must be opposite at the two distinct valleys, which can be observed from FIG.2 of ESI. Moreover, due to the existence of the horizontal mirror, they are fully spin-polarized in the out-of-plane direction (only $S_z$ component), which is confirmed by our calculated results with FIG.2 of ESI being only $S_z$ component. MSiGeN\textsubscript{4} (M=Mo and W) monolayers have conduction band valleys at K and K1. Although the VBM is not at the K/K1, the valleys are still well defined and not far in energy. The similar results can be observed in monolayer MoS\textsubscript{2}N\textsubscript{4}, WSi\textsubscript{2}N\textsubscript{4} and MoSi\textsubscript{2}As\textsubscript{3}\textsuperscript{34,35}.

The constant energy 2D contour plots of spin texture calculated in a $k_x-k_y$ plane centered at the Γ point are shown in Figure 5. The Rashba-type spin splitting of
We find that the band energies of the valence bands gives rise to the concentric spin-texture circles with clockwise and counterclockwise rotating spin directions, respectively. The concentric spin-texture circles are due to the pure 2D Rashba spin splitting in the valence bands. It is found that only in-plane Rashba spin splitting of the valence bands gives rise to the concentric spin-texture circles with clockwise and counterclockwise rotating spin up (red) and spin down (blue) electronic bands can be distinctly observed. The 2D Rashba spin splitting of valence bands along with applying uniaxial strain.

It is worth noting that the SOC component, which is also proved from Figure 2 of ESI. The elastic modulus with applying uniaxial strain.

FIG. 8. (Color online) The energy band gaps of MSiGeN\textsubscript{4} (M=Mo and W) monolayers as a function of $\frac{a_j}{a_0}$ (0.90-1.10) by using GGA+SOC.

The elastic modulus $C_{ij}$ can be attained. The carrier mobilities of MSiGeN\textsubscript{4} (M=Mo and W) monolayers are very higher than those of holes. The electron carrier mobilities of MoSiGeN\textsubscript{4} (WSiGeN\textsubscript{4}) along x and y directions are up to 5205 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1} (7047 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1}) and 6573 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1} (8768 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1}).

Next, we investigate the piezoelectric properties of MSiGeN\textsubscript{4} (M=Mo and W) monolayers. Performing symmetry analysis, due to a 3m point-group symmetry, the piezoelectric stress and strain tensors, and elastic tensor can be reduced into\textsuperscript{48}.

\begin{equation}
C = \begin{pmatrix}
C_{11} & C_{12} & 0 \\
C_{12} & C_{11} & 0 \\
0 & 0 & (C_{11} - C_{12})/2
\end{pmatrix}
\end{equation}

Here, the independent $d_{11}$ and $d_{31}$ are derived by $e_{ik} = d_{ij}C_{jk}$:

\begin{equation}
d_{11} = \frac{e_{11}}{C_{11} - C_{12}} \quad \text{and} \quad d_{31} = \frac{e_{31}}{C_{11} + C_{12}}
\end{equation}

For $e_{ij}$, the orthorhombic supercell of MSiGeN\textsubscript{4} (M=Mo and W) monolayers (in Figure 1) is adopted, and the calculated $e_{ij}$ and $d_{ij}$ are summarized in Table III, along with ones of MA\textsubscript{2}N\textsubscript{4} (M=Mo and W; A=Si and Ge) monolayer. With respect to the central M atomic plane, the MA\textsubscript{2}N\textsubscript{4} (M=Mo and W; A=Si and Ge) monolayer possess a reflection symmetry due to $D_{3h}$ symmetry, which leads to that they have only in-plane piezoelectricity. For MSiGeN\textsubscript{4} (M=Mo and W) monolayers, the difference in atomic sizes and electronegativities of the second and sixth layer atoms breaks the reflection symmetry.
TABLE II. For MSiGeN$_4$ (M=Mo and W) monolayers, elastic modulus ($C_{2D}$) using GGA, effective mass ($m^*$) and deformation potential ($E_l$) using GGA+SOC, carrier mobility ($\mu_{2D}$) at 300 K.

| Carrier type | $C_{2D}$ (Nm$^{-1}$) | $m^*$ | $E_l$ (eV) | $\mu_{2D}$ (cm$^2$V$^{-1}$s$^{-1}$) |
|--------------|----------------------|-------|-----------|--------------------------------------|
| MoSiGeN$_4$  |                      |       |           |                                      |
| Electrons    | x                    | 444.02| 0.41      | -3.37                                | 5205.14                             |
| Holes        | y                    | 444.02| 0.38      | -3.13                                | 6573.25                             |
| WSiGeN$_4$   |                      |       |           |                                      |
| Electrons    | x                    | 465.63| 0.30      | -4.06                                | 7046.80                             |
| Holes        | y                    | 465.63| 0.28      | -3.75                                | 8767.94                             |

TABLE III. Piezoelectric coefficients $e_{11}(d_{11})$ and $e_{31}(d_{31})$ of MSiGeN$_4$, MSi$_2$N$_4$ and MGe$_2$N$_4$ (M=Mo and W) monolayers, and the unit is $10^{-10}$C/m (pm/V).

| Name        | $e_{11}$ | $d_{11}$ | $e_{31}$ | $d_{31}$ |
|-------------|----------|----------|----------|----------|
| MoSi$_2$N$_4$ | 4.395    | 1.144    | 0.00     | 0.00     |
| MoSiGeN$_4$ | 5.116    | 1.494    | -0.087   | -0.014   |
| MoGe$_2$N$_4$ | 5.621    | 1.846    | 0.00     | 0.00     |
| WSi$_2$N$_4$ | 3.138    | 0.778    | 0.00     | 0.00     |
| WSiGeN$_4$ | 3.790    | 1.050    | 0.073    | 0.011    |
| WGe$_2$N$_4$ | 4.218    | 1.306    | 0.00     | 0.00     |

along the vertical direction, giving rise to a low degree of 3m symmetry. Therefore, both in-plane and vertical piezoelectricity are allowed in MSiGeN$_4$ (M=Mo and W) monolayers, when they are subject to a uniaxial in-plane strain. It is clearly seen that both $e_{11}$ and $d_{11}$ increase with increasing atomic mass from MSi$_2$N$_4$ (M=Mo and W) to MSiGeN$_4$ (M=Mo and W) to MGe$_2$N$_4$ (M=Mo and W). It is found that the MSiGeN$_4$ and MoA$_2$N$_4$ (A=Si and Ge) monolayers have higher $e_{11}/d_{11}$ values than WSiGeN$_4$ and WAg$_2$N$_4$ (A=Si and Ge) monolayers. For a given metal element M, the monolayers containing heavier column IV element have larger $e_{11}/d_{11}$ values. More significantly, the MSiGeN$_4$ (M=Mo and W) monolayers possess the vertical piezoelectric effect, which can be described by $e_{31}/d_{31}$. However, they are smaller by two orders of magnitude compared to $e_{11}/d_{11}$. Similar phenomenon can be observed in Janus MXY (M = Mo or W, X/Y = S, Se, or Te) monolayer.$^{48}$

VI. STRAIN EFFECTS

It has been proved that the electronic structures, topological properties, transport and piezoelectric properties of 2D materials can be effectively tuned by strain.$^{53-59}$ Here, we use $a/a_0$ to examine the effects of biaxial strain on the electronic structures of MSiGeN$_4$ (M=Mo and W) monolayers, where $a$ and $a_0$ are the strained and unstrained lattice constant with $a/a_0<1$ ($a/a_0>1$) being compressive (tensile) strain. The energy band structures of WSiGeN$_4$ with $a/a_0$ from 0.90 to 1.10 are plotted in Figure 7, and the related energy band structures are shown in FIG.4 of ESI for MoSiGeN$_4$. The energy band gaps of MSiGeN$_4$ (M=Mo and W) monolayers as a function of $a/a_0$ are shown in Figure 8. It is found that the energy band gap of MSiGeN$_4$ (M=Mo and W) monolayers firstly increases with increasing $a/a_0$, and then decreases. The up-and down trend of gap can also be observed in many 2D materials, like Janus TMD monolayers$^{60}$ and GeS$^{61}$. The compressive strain can make conduction band extrema (CBE) of WSiGeN$_4$ monolayer converge, especially for 0.96 and 0.98 strains. The conduction

FIG. 9. (Color online) For monolayer WSiGeN$_4$, the elastic constants $C_{ij}$ with the application of biaxial strain (0.90 to 1.10).
bands convergence is in favour of n-type Seebeck coefficient. The compressive strain can make K point become VBM, which is very useful for manipulating valley pseudospin. The compressive strain produces another effect that the CBM changes from K point to one point along K-Γ line. Similar strain effects on electronic structures of MoSiGeN$_4$ can be found. It is noted that MSiGeN$_4$ (M=Mo and W) monolayers in considered strain range are all semiconductors, which is useful for their piezoelectric application with strain.

The piezoelectric strain coefficients of MSiGeN$_4$ (M=Mo and W) monolayers are very small, and strain engineering may be an effective way to enhance their piezoelectric properties. Next, we consider the strain effects on piezoelectric properties of MSiGeN$_4$ (M=Mo and W) monolayers. The elastic constants ($C_{11}$, $C_{12}$, $C_{11}-C_{12}$ and $C_{11}+C_{12}$), piezoelectric stress coefficients ($e_{11}$ and $e_{31}$ along the ionic and electronic contributions), and piezoelectric strain coefficients ($d_{11}$ and $d_{31}$) of monolayer WSiGeN$_4$ as a function of biaxial strain are plotted in Figure 9, Figure 10 and Figure 11, respectively. For MoSiGeN$_4$, these are shown in FIG.5, FIG.6 and FIG.7 of ESI, respectively. With strain from 0.90 to 1.10, the $d_{11}$ increases due to decreased $C_{11}-C_{12}$ and enhanced $e_{11}$ based on Equation 8. At 10% strain, the $d_{11}$ of WSiGeN$_4$ (MoSiGeN$_4$) is 7.282 pm/V (8.081 pm/V), which is about seven times (five times) as large as unstrained one of 1.050 pm/V (1.494 pm/V). It is found that both ionic and electronic parts have positive contribution to $e_{11}$ with increasing tensile strain. Similar biaxial strain-enhanced $d_{11}$ can be observed in monolayer MoSi$_2$N$_4$, g-C$_3$N$_4$ and MoS$_2$. It is observed that the compressive strain can improve the $d_{31}$ (absolute value) of MSiGeN$_4$ (M=Mo and W) monolayers due to enhanced $e_{31}$ (absolute value), and the $d_{31}$ can be improved to 0.082 pm/V (-0.086 pm/V) for WSiGeN$_4$ (MoSiGeN$_4$) at 0.90 strain. Finally, it is found that theMSiGeN$_4$ (M=Mo and W) monolayers are mechanically stable in the considered strain range, based on calculated elastic constants satisfying the mechanical stability criteria.

VII. DISCUSSIONS AND CONCLUSION

The MSi$_2$N$_4$ (M = Mo, W) monolayers have been recently synthesized, which are grown by passivating the surface dangling bonds of MN$_2$ (M = Mo, W) layer with Si-N tetrahedra when introducing elemental Si$^{30}$. Thus, it is possible to achieve Janus MSiGeN$_4$ (M=Mo and W) monolayers by simultaneously introducing Si and Ge elements during CVD growth of nonlayered MN$_2$ (M = Mo, W) to passivate its surface. Compared to MSi$_2$N$_4$ (M...
Mo, W) monolayers, the most important difference is that Janus MSiGeN₄ (M=Mo and W) monolayers have out-of-plane piezoelectric polarization and Rashba effect due to their out-of-plane asymmetry. Although their out-of-plane piezoelectric polarization and Rashba effect are very weak, our works open a new avenue to achieve Janus materials in the new 2D MA₂Z₄ family.

In summary, we investigate the electronic structures, carrier mobilities, piezoelectric properties of MSiGeN₄ (M=Mo and W) monolayers by the reliable first-principle calculations. They are found to exhibit mechanical, thermodynamical and dynamic stability, and high experimental feasibility. It is found that MSiGeN₄ (M=Mo and W) monolayers are indirect gap semiconductors. When the SOC is considered, the Rashba effect can be observed in the valence bands of MSiGeN₄ (M=Mo and W) monolayers. Their electron mobilities are very high due to very light electron effective masses. The $e_{11}/d_{11}$ of MSiGeN₄ (M=Mo and W) monolayers can be induced by a uniaxial strain in the basal plane, similar to MSi₂N₄ (M = Mo, W) monolayers. In addition to this, a vertical piezoelectric polarization $e_{31}/d_{31}$ can be produced upon application of uniaxial or biaxial strains due to the lack of reflection symmetry with respect to M atomic layer. Calculated results show that compressive strain can change the positions of CBM and VBM of MSiGeN₄ (M=Mo and W) monolayers, and tune the strength of conduction bands convergence. It is also found that biaxial strain can enhance $d_{11}$ [$d_{31}$ (absolute values)] of MSiGeN₄ (M=Mo and W) monolayers by tensile [compressive] strain. Our works will stimulate further experimental studies to achieve MSiGeN₄ (M=Mo and W) monolayers, and will motivate farther exploration on Janus monolayers in new 2D MA₂Z₄ family.

Conflicts of interest
There are no conflicts to declare.

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