Tuning electronic structures, transport and piezoelectric coefficients of monolayer MoSi$_2$N$_4$ with biaxial strain

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Experimentally synthesized MoSi$_2$N$_4$ (Science 360, 670-674 (2020)) is a piezoelectric semiconductor. Here, we systematically study the large biaxial strain effects (-10% to 10%) on electronic structures, transport and piezoelectric coefficients of monolayer MoSi$_2$N$_4$ by density functional theory (DFT). With $a/a_0$ from 0.90 to 1.10, the energy band gap firstly increases, and then decreases. The compressive strain can change relative position and numbers of conduction band extrema (CBE), and then the strength of conduction bands convergence can be enhanced, to the benefit of n-type $ZT_e$. Only about -4% strain can effectively improve n-type $ZT_e$. Calculated results show that the increasing tensile strain can increase piezoelectric stress coefficient $e_{11}$, and simultaneously reduce the elastic coefficient $C_{11}$-$C_{12}$, which gives rise to improved piezoelectric strain coefficient $d_{11}$. The tensile strain-induced enhanced $e_{11}$ is due to the synchronously improved ionic and electronic contributions. With respect to unstrained one, the $d_{11}$ at 10% strain can be improved by 485%. Our works imply that strain can effectively tune the electronic structures, transport and piezoelectric coefficients of monolayer MoSi$_2$N$_4$, and can motivate farther experimental exploration.

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I. INTRODUCTION

The successful exfoliation of graphene$^1$ induces increasing attention on two-dimensional (2D) materials. Many of them have semiconducting behaviour, which has various potential application in electronics, optoelectronics and piezoelectronics$^2$-5. Their electronic structures, heat transport and piezoelectric properties have been widely investigated$^6$-16. It has been proved that the strain can effectively tune electronic structures, transport and piezoelectric properties of 2D materials$^{15}$-23, which shows great potential for better use in the nanoelectronic, thermoelectric and piezoelectric applications. For example, both compressive and tensile strain can induce the semiconductor to metal transition in monolayer MoS$_2$17. In many transition metal dichalcogenides (TMD) monolayers, the power factor can be enhanced by strain due to bands converge$^{15}$-$26$. With increased tensile strain, the lattice thermal conductivity shows monotonous decrease, up-and-down and jump behavior with similar penta-structures$^{19}$. Strain can also improve the piezoelectric strain coefficient by tuning the elastic and piezoelectric stress coefficients$^{20}$-$23$. Recently, the layered 2D MoSi$_2$N$_4$ has been experimentally achieved by chemical vapor deposition (CVD)$^{24}$. The septuple-atomic-layer MA$_2$Z$_4$ monolayers with twelve different structures are constructed by intercalating MoS$_2$-type MZ$_2$ monolayer into InSe-type A$_2$Z$_2$ monolayer$^{25}$. The 66 thermodynamically and dynamically stable MA$_2$Z$_4$ are predicted by the first principle calculations. They can be common semiconductor, half-metal ferromagnetism or spin-gapless semiconductor, Ising superconductor and topological insulator, which depends on the number of valence electrons$^{25}$. We predict intrinsic piezoelectricity in monolayer MA$_2$Z$_4$,$^{26}$ which means that MA$_2$Z$_4$ family may have potential application in piezoelectric field.

In nanoscale devices, the residual strain usually exists in real applications$^{27}$. In our previous work, the small strain effects (-4% to 4%) on piezoelectric coefficients of monolayer MoSi$_2$N$_4$ have been investigated$^{28}$. In this work, the large (-10% to 10%) biaxial strain-tuned electronic structures, transport and piezoelectric coefficients of monolayer MoSi$_2$N$_4$ are studied by the first principle calculations. With $a/a_0$ from 0.90 to 1.10, the energy band gap of monolayer MoSi$_2$N$_4$ firstly increases, and then decreases. In n-type doping, the Seebeck coefficient S can be effectively enhanced by applying compressive strain, and then the $ZT_e$ can be improved. The tensile strain can induce flat valence bands around the $\Gamma$ point near the Fermi level, producing large p-type S. Calculated results show that tensile strain can improve the only independent piezoelectric constants $d_{11}$ due to reduced $C_{11}$-$C_{12}$ and enhanced $e_{11}$. At tensile strain of 10%, the $d_{11}$ can be improved to 6.73 pm/V, which is compared to one of most TMD monolayers$^{10,12}$. Therefore, our works

![FIG. 1. (Color online)The crystal structure of monolayer MoSi$_2$N$_4$ ((a) side view and (b) top view). The primitive cell is are marked by black line, and the large red balls represent Mo atoms, and the middle blue balls for Si atoms, and the small green balls for N atoms.](Image 340x404 to 539x475)
FIG. 2. (Color online) The energy band structures of monolayer MoSi$_2$N$_4$ using GGA+SOC with the application of biaxial strain (-10% to 10%), and the unstrained energy band using GGA.

FIG. 3. (Color online) For MoSi$_2$N$_4$ monolayer, the energy band gap and spin-orbit splitting value $\Delta$ at K point using GGA+SOC as a function of strain.

give an experimental proposal to improve transport and piezoelectric coefficients of monolayer MoSi$_2$N$_4$.

The rest of the paper is organized as follows. In the next section, we shall give our computational details and methods about transport and piezoelectric coefficients. In the third, fourth and fifth section, we will present main results of monolayer MoSi$_2$N$_4$ about strain-tuned electronic structures, transport and piezoelectric coefficients. Finally, we shall give our conclusions in the sixth section.

II. COMPUTATIONAL DETAIL

To avoid interactions between two neighboring images, a vacuum spacing of more than 32 Å along the z direction is added to construct monolayer MoSi$_2$N$_4$. The elastic stiffness tensor $C_{ij}$ and the piezoelectric stress coefficients $e_{ij}$ are calculated by using strain-stress relationship (SSR) and density functional perturbation theory (DFPT) method$^{28}$, which are performed by using the VASP code$^{29-31}$ within the framework of DFT$^{32}$. A ki-
nnetic cutoff energy of 500 eV is adopted, and we use the popular generalized gradient approximation of Perdew, Burke and Ernzerh (GGA-PBE) as the exchange-correlation potential to calculate piezoelectric and elastic properties. The total energy convergence criterion is set to $10^{-8}$ eV, and the Hellmann-Feynman forces on each atom are less than 0.0001 eVÅ$^{-1}$. The Brillouin zone (BZ) sampling is done using a Monkhorst-Pack mesh of $15\times15\times1$ for $C_{ij}$, and $9\times16\times1$ for $\epsilon_{ij}$. The 2D elastic coefficients $C_{ij}^{2D}$ and piezoelectric stress coefficients $\epsilon_{ij}^{2D}$ have been renormalized by the the length of unit cell along z direction ($L_z$): $C_{ij}^{2D} = L_z C_{ij}^{3D}$ and $\epsilon_{ij}^{2D} = L_z \epsilon_{ij}^{3D}$.

The electronic transport coefficients of MoSi$_2$N$_4$ monolayer are calculated through solving Boltzmann transport equations within the constant scattering time approximation (CSTA), which is performed by BoltzTrap code. To include the spin orbital coupling (SOC), a full-potential linearized augmented-plane-waves method is used to calculate the energy bands of MoSi$_2$N$_4$ monolayer, as implemented in the WIEN2k package. To attain accurate transport coefficients, a $35 \times 35 \times 1$ k-point mesh is used in the first BZ for the energy band calculation, make harmonic expansion up to $l_{max} = 10$ in each of the atomic spheres, and set $R_{int} \ast k_{max} = 8$.

III. ELECTRONIC STRUCTURES

The MoSi$_2$N$_4$ monolayer can be considered as the insertion of the 2H MoS$_2$-type MoN$_2$ monolayer into the α-InSe-type Si$_2$ N$_2$, and the side and top views of the structure of the MoSi$_2$N$_4$ monolayer are plotted in Figure 1. Using optimized lattice constants, the energy bands of MoSi$_2$N$_4$ monolayer using GGA and GGA+SOC are shown in Figure 2, and exhibit both the indirect band gaps with valence band maximum (VBM) at Γ point and conduction band minimum (CBM) at K point. Due to lacking inversion symmetry and containing the heavy element Mo, there exists a SOC induced spin splitting of about 0.15 eV near the Fermi level in the valence bands at K point. This may provide a platform for spin-valley physics, but the VBM is not at K point, which can be tuned by strain.

It is proved that the electronic structures, topological properties, transport and piezoelectric properties of 2D materials can be effectively tuned by strain. The biaxial strain can be simulated by $a/a_0$ or $(a-a_0)/a_0$, where $a$ and $a_0$ are the strained and unstrained lattice constant, respectively. The $a/a_0<1$ or $(a-a_0)/a_0<0$ means compressive strain, while $a/a_0>1$ or $(a-a_0)/a_0>0$ implies tensile strain. With $a/a_0$ from 0.90 to 1.10, the energy band structures are plotted in Figure 2, and the energy band gap and spin-orbit splitting value $\Delta$ at K point are shown in Figure 3. It is found that the energy band gap firstly increases (0.90 to 0.96), and then decreases (0.96 to 1.10). Similar phenomenon can be observed in many TMD and Janus TMD monolayers.

With strain from compressive one to tensile one, the $\Delta$ has a rapid increase, and then a slight decrease. The position of CBM (VBM) changes from K (Γ) point to one point along the K-Γ direction (K point), when the compressive strain reaches about 0.94 (0.98). The compressive strain can also tune the numbers and relative positions of valence band extrema (VBE) or CBM. For example, at 0.96, the four CBE can be observed, and they energies are very close, which has very important effects on transport properties. At 0.98, the energy of two VBE are nearly the same. The compressive strain make spin splitting at K point to be VBM, which is very useful to allow spin manipulation for spin-valley physics. For example, at 0.94 strain, the VBM at K point is 0.49 eV higher than that at Γ point. It is clearly seen that the increasing tensile strain can make valence band around the Γ point near the Fermi level more flat.

IV. ELECTRONIC TRANSPORT PROPERTY

Proposed by Hicks and Dresselhaus in 1993, the potential thermoelectric materials can be achieved in the low-dimensional systems or nanostructures. The dimensionless figure of merit, $ZT = S^2\sigma T/(\kappa_e + \kappa_L)$, can be used to measure the efficiency of thermoelectric conversion of a thermoelectric material, where $S$, $\sigma$, $T$, $\kappa_e$ and $\kappa_L$ are the Seebeck coefficient, electrical conductivity, working temperature, electronic and lattice thermal conductivities, respectively. It is noted that, for the 2D material, the calculated $\kappa_e$ and $\kappa_L$ depend on $L_z$ (here, $L_z=40$ Å), and the $S$ and $ZT$ is independent of $L_z$. It is proved that the SOC has important effects on transport coefficients of TMD and Janus TMD monolayers. However, the SOC has neglectful influences on transport properties of unstrained MoSi$_2$N$_4$ monolayer, which can be observed from typical Seebeck coefficient $S$ in Figure 4. This is because the energy bands near the Fermi level between GGA and GGA+SOC is nearly the same. However, the SOC has an effect on p-type transport coefficients with the condition of compressive strain, for example at 0.96 strain, which is because the SOC can re-
FIG. 5. (Color online) For MoSi$_2$N$_4$ monolayer, the room-temperature transport coefficients with the $a/a_0$ from 0.90 to 1.10 [(Left): compressive strain and (Right): tensile strain]: Seebeck coefficient $S$, electrical conductivity with respect to scattering time $\sigma/\tau$, power factor with respect to scattering time $S^2\sigma/\tau$ and $ZT_e$ (an upper limit of $ZT$) as a function of doping level ($N$) using GGA+SOC.

move the band degeneracy near the VBM. So, the SOC is included to investigate the biaxial strain effects on transport coefficients of MoSi$_2$N$_4$ monolayer.

Using GGA+SOC, the room temperature $S$, $\sigma/\tau$ and $S^2\sigma/\tau$ of MoSi$_2$N$_4$ monolayer under different strain (0.90 to 1.10) are shown in Figure 5. It is clearly seen that the compressive strain has important effects on $S$, especially for n-type doping. However, the tensile strain produces small influences on $S$, especially for n-type $S$. These can be explained by strain-induced energy bands. When the strain is less than or equal to about 0.98, the n-type $S$ (absolute value) can be observably improved, which is
due to compressive strain-driven accidental conduction band degeneracies, namely bands convergence. With expanding compressive strain, in the low doping, the p-type S firstly increases, and has almost no change. This is because the valence bands convergence can be observed at about 0.98, and then is removed. For considered tensile strain, the conduction bands near the Fermi level have little change, which leads to almost unchanged n-type S. When the strain changes from 1.00 to 1.10, the p-type S increases, which is due to tensile strain-induced more flat valence bands around Γ point near the Fermi level. This can be understood by $S = \frac{10^4}{54x70}$, which is found that the compressive strain can dramatically improve $S$. It is found that the strain-induced bands convergence improves $S$, which will lead to improved $S$. The temperature and carrier concentration, respectively. The flat bands can produce very large effective mass of the carrier, which will lead to improved $S$. It is found that the strain has nearly the opposite effects on $\sigma/\tau$ with respect to $S$. It is found that the compressive strain can dramatically improve $S$, which will lead to improved $S$. An upper limit of $ZT$ can be measured by $ZT_e = S^2/\sigma/\tau \kappa_e$, neglecting the $\kappa_L$. The room temperature $ZT_e$ of MoSi$_2$N$_4$ monolayer under different strain as a function of doping level are also shown in Figure 5. Calculated results show that the dependence of $ZT_e$ is very similar to one of S (absolute value), which can be explained by the Wiedemann-Franz law: $\kappa_e = L\sigma T$ ($L$ is the Lorenz number). And then the $ZT_e$ can be reformulated by $ZT_e = S^2/L$. Thus, the strain-induced bands convergence improves $S$, which is beneficial to better $ZT_e$.

V. PIEZOELECTRIC PROPERTY

Employing Voigt notation, the elastic, piezoelectric stress and strain tensors $(C_{ij}, e_{ij}$ and $d_{ij})$ of monolayer MoSi$_2$N$_4$ with the point group 6m2 become:

\[
\begin{pmatrix}
 e_{11} & e_{11} & 0 \\
 0 & 0 & -e_{11} \\
 0 & 0 & 0
\end{pmatrix} \\
\begin{pmatrix}
 d_{11} & -d_{11} & 0 \\
 0 & 0 & -2d_{11}
\end{pmatrix} \\
\begin{pmatrix}
 C_{11} & C_{12} & 0 \\
 C_{12} & C_{11} & 0 \\
 0 & 0 & C_{11} - C_{12}
\end{pmatrix}
\]

The $e_{ik}$ is related with $d_{ij}$ by $e_{ik} = d_{ij}C_{jk}$. Solving the equations, the only independent in-plane $d_{11}$ is:

\[
d_{11} = \frac{e_{11}}{C_{11} - C_{12}}
\]

For monolayer MoSi$_2$N$_4$, the independent elastic stiffness coefficients of $C_{11}$ and $C_{12}$ (536.97 N/m and 152.98 N/m) are calculated, and one independent $e_{11}$ ($4.40 \times 10^{-10}$ C/m) is attained by DFPT. By Equation 4, the predicted $d_{11}$ is 1.15 pm/V, which is smaller than one of most 2D TMD monolayers. So, the biaxial strain (-10% to 10%) is considered to improve the $d_{11}$ of monolayer MoSi$_2$N$_4$. The elastic constants $C_{11}, C_{12}, C_{11}-C_{12}$, piezoelectric coefficients $e_{11}$ (including ionic and electronic contribution) and $d_{11}$ as a function of biaxial strain are shown in Figure 6. In considered strain range, all calculated $C_{11}$ and $C_{12}$ meet the Born criteria of mechanical stability. With -10% to 10%, it is clearly seen that the $C_{11}, C_{12}$ and $C_{11}-C_{12}$ decreases, which is in favour of the improved $d_{11}$. The $C_{11}-C_{12}$ ranges from...
When the strain changes from -10% to 10%, the $e_{11}$ increases from $-1.14 \times 10^{-10}$ C/m to $15.09 \times 10^{-10}$ C/m, which also makes for enhanced $d_{11}$. From negative value to positive value for $e_{11}$, the direction of polarization produces reverse. It is found that the ionic contribution to $e_{11}$ changes from negative value to positive value at about 8% strain, which will lead to superposed effect to $e_{11}$ with electronic contribution.

When the strain is less than about -8%, the absolute value of the ionic contribution to $e_{11}$ is larger than electronic one, which gives rise to minus $e_{11}$. It is clearly seen that the $d_{11}$ changes from minus value to positive value with the strain being larger than -8%, which is due to the change of $e_{11}$. Calculated results show that tensile strain can improve the $d_{11}$ of monolayer MoSi$_2$N$_4$. At 10% strain, the $d_{11}$ becomes 6.73 pm/V from unstrained 1.15 pm/V, increased by 485%. Similar phenomenon can be observed in monolayer g-C$_3$N$_4$ and MoS$_2$ with the same point group$^{23}$. Thus, strain can effectively enhance $d_{11}$ of MoSi$_2$N$_4$ monolayer.

VI. CONCLUSION

In summary, we investigate the biaxial strain (-10% to 10%) effects on electronic structures, transport and piezoelectric coefficients of monolayer MoSi$_2$N$_4$ by the reliable first-principles calculations. With the strain from 0.90 to 1.10, the energy band gap of MoSi$_2$N$_4$ monolayer shows a nonmonotonic behavior. It is found that the SOC has little effects on transport coefficients of unstrained MoSi$_2$N$_4$ in considered doping range due to the hardly changed dispersion of bands near the Fermi level. Calculated results show that compressive strain can tune the numbers and relative positions of CBE, which can lead to enhanced n-type S, and then better n-type $ZT$. Compared to unstrained one, tensile strain can improve the $d_{11}$ of MoSi$_2$N$_4$ monolayer due to enhanced $e_{11}$ and reduced $C_{11}-C_{12}$. Calculated results show that both ionic and electronic contributions to $e_{11}$ with increasing tensile strain is in favour of the enhanced $d_{11}$. Our works may provide an idea to optimize the electronic structures, transport and piezoelectric properties of monolayer MoSi$_2$N$_4$.

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