1. INTRODUCTION

Two-dimensional transition-metal dichalcogenides (2D-TMDs) alloys have been heavily studied owing to their diverse applications in nanoelectronics, optoelectronic devices, as well as energy harvesting and so on.\(^\text{6}\)\(^\text{13}\)\(^\text{15}\) These materials belong to layered structures, and the band structures vary from semiconducting to semimetallic with combinations of elemental composition.\(^\text{6}\) Among them, the sulﬁde TMDs (MS\(_2\)) (M = Mo, W) are used in the wide-ranging fabrications of optoelectronic nanodevices, high responsive photodetectors, and transistors because of their large bandgap of 1–2 eV, high on/off ratio (∼10\(^\text{3}\)), and room-temperature mobility of >200 cm\(^2\) V\(^{-1}\) s\(^{-1}\).\(^\text{14}\)\(^\text{18}\)\(^\text{22}\) Furthermore, to integrate MS\(_2\) for advanced applications, many possibilities have been employed to extend the related material properties by external means, such as strain,\(^\text{11}\)\(^\text{12}\)\(^\text{15}\)\(^\text{16}\)\(^\text{17}\)\(^\text{21}\)\(^\text{22}\)\(^\text{24}\)\(^\text{26}\)\(^\text{27}\) and external fields.\(^\text{13}\)

Recently, alloying semiconductors provide an avenue to achieve continuously tunable band structure, carrier mobility, and effective mass, as reported by both theory and experiment for Mo\(_{1−x}\)W\(_x\)S\(_2\)\(^\text{12}\)\(^\text{14}\)\(^\text{15}\)\(^\text{16}\)\(^\text{17}\) and the negative values of mixing enthalpy mean that Mo\(_{1−x}\)W\(_x\)S\(_2\) has good thermodynamic stability at room temperature. However, these methods are ﬁnite and irreversible for the band structures and band offsets. In particular, external pressure can also be used as an effective method to modulate the relevant physical and chemical properties of 2D materials, and some achievements have been obtained, for example, MoS\(_2\) and WS\(_2\) monolayer, bilayer, and the corresponding bulk counterparts can undergo a semiconductor-to-metal transition under the condition of pressure.\(^\text{19}\)\(^\text{−}\)\(^\text{34}\) Under the condition of hydrostatic pressure, the compressive rate in the direction of out-of-plane was significantly higher than that of in-plane because of their unique layered structures due to the strong intralayer ionic-covalent bonds and the weak interlayer van der Waals (vdW) interactions.\(^\text{19}\)\(^\text{−}\)\(^\text{22}\)\(^\text{24}\)\(^\text{26}\)\(^\text{27}\) On the other hand, the electronic properties have also been changed under hydrostatic pressure.\(^\text{21}\)\(^\text{22}\)\(^\text{24}\)\(^\text{27}\)\(^\text{31}\)\(^\text{−}\)\(^\text{34}\) Especially, the bandgap of bulk TMDs was found to be reduced consequently and to become metallic with increasing pressure, whereas the bandgap of the monolayer gradually increased in the small pressure range.\(^\text{21}\)\(^\text{22}\)\(^\text{31}\)\(^\text{32}\) Importantly, the evolution of band structure combined modulation of composition and number of layers under hydrostatic pressure has gained an increased interest. However, for the aspect of theoretical method at the atomic level, the role of hydrostatic pressure on the band evolution in Mo\(_{1−x}\)W\(_x\)S\(_2\) is still lacking. Therefore, it is necessary to address the related underlying mechanism in TMD alloys, including (i) the variation of bond identities involved in bond length, bond energy, and bond angle with the composition and pressure, (ii) the relationship between number of layers and bandgap under pressure, and (iii) the origin of pressure-dependent semiconductor-to-metal transitions under different composition and number of layers.
2. PRINCIPLE

Structurally, layered material, Mo\((1-x)\)W\(_x\)S\(_2\) consists of intralayer ionic-covalent bonds and is stacked with interlayer vdW interaction. Notably, each layer contains a single layer of metal atoms and two planes of dichalcogenide atoms and thus forms a sandwiched structure, which are coordinated through ionic-covalent interactions. The intralayer bonding of M–S in each S–M–S trilayer is strong, and the weak vdW force exists at the interlayer. For the case of a Mo\((1-x)\)W\(_x\)S\(_2\) with number of layers \(n\), the total energy can be expressed as

\[
U_{\text{total}} = n U_{\text{intra}} + n U_{\text{dis}} + (n - 1) U_{\text{inter}}
\]

(1)

where \(U_{\text{intra}}\) and \(U_{\text{inter}}\) are the M–S potential of intralayer and interlayer interactions, respectively, \(U_{\text{dis}}\) is the distortion energy originally from the lattice mismatch of Mo\(_2\)S\(_2\) and WS\(_2\). Conventionally, the potential function of Born–Mayer–Huggins-type was employed to consider the ionic, covalent, and weak vdW interactions among atoms, and which has been successfully applied to various ionic solid materials.\(^{35,36}\)

\[
U_{\text{total}} = \sum_i \sum_j \left[ \frac{Z_i Z_j e^2}{r_{ij}} + A_{ij} \exp\left( \frac{\sigma_{ij} - r_{ij}}{\rho_{ij}} \right) - C_{ij} \right] + \sum_i \sum_j D_{ij} \left[ 1 - \exp\left( - \alpha_{ij} (r_{ij} - r_0) \right) \right] + \sum_\varphi k_\varphi (\varphi - \varphi_0)
\]

(2)

The first term represents the Coulomb potential \((Z\) is the atomic charge on atom \(i\) or \(j\), and \(e\) is the elementary electric charge, \(r_{ij}\) is the interactions distance), and the second and third terms correspond to the short-rang exchange repulsion potential and the dipole–dipole vdW dispersive interactions \((A_{ij}, \sigma_{ij}, \rho_{ij}\) are the constants for each atom pair, and \(C_{ij}\) is the constant for each atom), respectively. The fourth and fifth, respectively, correspond to the More-type and angle potentials \((D_{ij}, k_{ij}, \sigma_{ij}\) are the bond potential parameters, \(\varphi\) is the bending angle, \(r_{ij}\) and \(r_0\) are the distance and angle of atoms at minimum energy, respectively), which are the covalent interactions. The interaction potentials of intralayer are employed by More-type, angle, and Coulomb potentials.\(^{37,38}\)

The atomic interaction of interlayer corresponds to the Coulomb, short-range exchange repulsion, and vdW potential.\(^{36}\)

In the case of intralayer M–S bond (using \(d_{ij}\) to describe the M–S bond length), the interaction potential between M and S consists of bond stretching, \(U_{\text{bond}}\), bond angle variation, \(U_{\text{angle}}\), and Coulomb electrostatic potential, \(U_{\text{coul}}\).\(^{37,38}\) Thus, we have

\[
U_{\text{intra}} = \sum U_{\text{bond}} + \sum U_{\text{angle}} + \sum U_{\text{coul}}
\]

(3)

Here, \(U_{\text{bond}} = D \times [1 - e^{-\alpha(d_{ij} - d_0)^2}], U_{\text{angle}} = \frac{k_\theta}{2} \theta^2 + \frac{k_\psi}{2} \psi^2\), and \(U_{\text{coul}} = C \frac{q_i q_j}{r_{ij}}\), where \(k_\theta\) and \(k_\psi\) are the bond potential parameters. It is found that the force constant is almost the same for Mo\(_2\)S\(_2\) and WS\(_2\), and thus, the parameters should be approximately equal. In our case, we take \(D = 19.945, \alpha = 0.858, k_\theta = 0.9387,\) and \(k_\psi = 0.8631\) as the representative values in our calculations.\(^{39,40}\)

Thus, the interlayer energy of each S atom is\(^{36,48}\)

\[
U_{\text{inter}} = \sum U_{\text{rep}} + \sum U_{\text{vdW}} + \sum U_{\text{coul}}
\]

(4)

Here, \(U_{\text{rep}} = A_{ij} \exp\left( \frac{\sigma_{ij} - \rho_{ij}}{\rho_{ij}} \right)\), \(U_{\text{vdW}} = -\frac{C}{r^6}\), and \(U_{\text{coul}} = \frac{2Z_i Z_j e^2}{r}\), where \(i\) and \(j\) are the S atoms of adjacent layers. The constants of S–S include \(A_{ij} = 0.00714\) eVÅ, \(\sigma_{ij} = 0.17\) Å, \(\rho_{ij} = 3.66\) Å, and \(C = 49.19\) eVÅ\(^3\).\(^{38}\) Therefore, the variation of energy in the intralayer under the approach of pressure is \(\Delta U_{\text{intra}}\) and \(\Delta U_{\text{inter}}\) respectively. Combining the interactions from intralayer and interlayer, the variation of average single bond energy in the system induced by hydrostatic pressure can be obtained as

\[
\Delta E = \frac{1}{N z_n} \left[ \Delta U_{\text{intra}} + \frac{(n - 1) \Delta U_{\text{inter}}}{3n} \right]
\]

(5)

where \(N\) is the number of atoms, and \(z_n\) is the layer number dependence of coordination number (CN). Notably, the effective CN of monolayer, bilayer, and bulk MS\(_2\) are 4, 6, and 12, respectively.\(^{39,40}\)

Physically, the cohesive energy is \(E_C = z_n E_{\text{rep}}\), where \(E_C\) and \(E_{\text{rep}}\) are the cohesive energy and single bond energy, respectively. Subsequently, the cohesive energy of the system under hydrostatic pressure is

\[
E_C(x, p, n) = Nz_n[(1 - x)E_{\text{rep}} + xE_{\text{rep}} + \Delta E]
\]

(6)

where \(E_{\text{rep}}^a\) and \(E_{\text{rep}}^b\) are the layer number dependence of single bond energy in Mo\(_2\)S\(_2\) and WS\(_2\) respectively. According to the atomic-bond-relaxation (ABR) correlation mechanism,\(^{50–52}\) a
the lattice parameter, \( a \), and the bond length, \( d \), decrease slightly with increasing pressure. Moreover, the lattice parameter and M–S bond length of MoS\(_2\) (WS\(_2\)) reveal a linear decrease under hydrostatic pressure with a rate of 0.0107 and 0.004 Å/GPa (0.0006 and 0.0023 Å/GPa), respectively. It is also found that the thickness of intralayer defined by S–S distance increases slightly under pressure due to the Poisson effect (see Figure 2b). In addition, the change of intralayer bond parameters results in the increase of in-plane angle, \( \theta \), whereas decrease of out-of-plane angle, \( \psi \) under pressure (see Figure 2d,e). Notably, the interlayer \( t \) decreases strongly under pressure, reflecting the weak vdW interaction of interlayer, and shrinks abruptly with pressure especially below 20 GPa (see Figure 2f). Obviously, our predictions are consistent with the first-principles calculations.\(^{26,27}\)

Moreover, the composition-dependent elastic modulus of Mo\(_{(1-x)}\)W\(_x\)S\(_2\) in the interlayer can be expressed as:

\[
Y_{\text{int}}(x) = \left(1 - x\right)Y(MoS_2) + xY(WS_2)
\]

where \( Y \) is the elastic modulus of MS\(_2\). The interlayer elastic moduli of Mo\(_2\) in x- and y-directions are 200.3, 197.8, and 511 GPa, whereas those x- and y-directions of WS\(_2\) are 218 and 211 GPa, respectively.\(^{55,56}\) Also, we can get the elastic modulus in the z-direction through the relationship: \( Y_z(MoS_2)/Y_z(WS_2) = Y_z(MoS_2)/Y_z(MoS_2) \) and that in the z-direction of WS\(_2\) is equal to 545 GPa. Ghorbani-Asl et al.\(^{56}\) indicated that the stress–strain relation curves of monolayer MS\(_2\) satisfy the Hooke’s law, and the uniaxial tensile strain can reach up to 19%.

Moreover, the elastic modulus in the interlayer can be obtained by taking the second derivative of the interlayer interaction, that is, \( Y_{\text{inter}}(t) = \Gamma \frac{d^2t_{\text{inter}}}{dt^2} \), where \( \Gamma \) is the number of atoms in a unit area, and in our calculation, we take \( \Gamma = 11/nm^2 \). Therefore, we have the change of bond parameters under hydrostatic pressure:

\[
\begin{align*}
\left|a(x)\right| &= a_{0}(x) - \frac{a_{0}(x)\left(1/Y - \eta Y + v_{\parallel} / Y_{\parallel}\right)}{1 + \frac{3}{2}(B' - 4)\left(\xi^{2/3} - 1\right)} \quad \text{intralayer} \\
\left|b(x)\right| &= b_{0}(x) - \frac{b_{0}(x)\left(1/Y - \eta Y + v_{\perp} / Y_{\perp}\right)}{1 + \frac{3}{2}(B' - 4)\left(\xi^{2/3} - 1\right)} \quad \text{intralayer} \\
\left|c(x)\right| &= c_{0}(x) - \frac{c_{0}(x)\left(1/Y - \eta Y + v_{\perp} / Y_{\perp}\right)}{1 + \frac{3}{2}(B' - 4)\left(\xi^{2/3} - 1\right)} \quad \text{intralayer}
\end{align*}
\]

where \( v_{\parallel} \) and \( v_{\perp} \) are the Poisson’s ratio in the in-plane and out-of-plane of intralayer. Note that the \( v_{\parallel} = 0.21 \) and \( v_{\perp} = 0.27 \) for the Mo\(_{(1-x)}\)W\(_x\)S\(_2\).\(^{55,58,59}\)

Figure 3 shows the change of unit cell volume in Mo\(_{(1-x)}\)W\(_x\)S\(_2\) at the composition of \( x = 0, 0.5 \), and 1 as a function of pressure with the bulk, bilayer, and monolayer, respectively. In general, the relationship between volume and pressure is described by the third-order Birch–Murnaghan equation:\(^{60,61}\)

\[
p(V) = \frac{3B}{2}(\xi^{-2/3} - \xi^{-5/3})\left\{1 + \frac{3}{2}(B' - 4)(\xi^{2/3} - 1)\right\}
\]

where \( B \) and \( B' \) are the bulk modulus and its first-order pressure derivative, \( \xi = V/V_0 \) is the ratio of volume addressed after and before being compressed, and \( V_0 \) represents the volume under ambient pressure, \( V \) is the pressure-dependent unit cell volume, and \( V = a(x)b(x)\left(1/a(x) + (n - 1)/t\right) \).

Notably, the composition-dependent bulk modulus can be described by: \(^{62}\)

\[
B(x) = \left[\left(1 - x\right)a_B + x\right]B_0 / a(x).
\]

Evidently, in Figure 3, we see that the change of volume is large due to weak...
interlayer interaction.\textsuperscript{19−21,23,24} Also, we obtain the bulk modulus of MoS\(_2\) (WS\(_2\)), which is 57.92 ± 0.98 GPa (59.68 ± 2.47 GPa) with its first pressure derivation, \(B' = 3.59 ± 0.06\) GPa (3.69 ± 0.15 GPa). Our results agree with the related experimental measurements and theoretical calculations.\textsuperscript{19,20,24} Nayak et al.\textsuperscript{21} and Chi et al.\textsuperscript{24} reported that the bulk moduli of bulk MoS\(_2\) are 57 GPa and 57.86 ± 0.30 GPa with \(B'\) being 4.6 and 5.28 ± 0.01 GPa, respectively. Selvi et al.\textsuperscript{20} revealed that the bulk modulus of bulk WS\(_2\) is \(B = 61 ± 1\) GPa with \(B' = 9.0 ± 0.3\) GPa. A similar method is used with Mo\(_{(1-x)}\)W\(_x\)S\(_2\) with the monolayer and bilayer, and the results are shown in Figure 3d. Moreover, the corresponding values are listed in Table 1. Importantly, the bulk modulus of monolayer Mo\(_{(1-x)}\)W\(_x\)S\(_2\) is larger than that of the bilayer and bulk counterparts because the monolayer has only strong covalent bonds and lacks weak vDW bonds. Also, the bulk modulus of Mo\(_{(1-x)}\)W\(_x\)S\(_2\) has an approximately linear increase with increasing composition due to similar lattice parameters of MoS\(_2\) and WS\(_2\).

Figure 4 shows the various kinds of energy change in Mo\(_{(1-x)}\)W\(_x\)S\(_2\) with different layers under the condition of hydrostatic pressure. Especially, the distortion energy in Mo\(_{(1-x)}\)W\(_x\)S\(_2\) expresses a dramatic increase and then decrease with increasing \(x\), and it can be attributed to the bond mismatch of MoS\(_2\) and WS\(_2\). Notably, the red points in the figure are the results of our calculations when the composition equals to 0, 1/3, 2/3, and 1, respectively. Therefore, the composition-dependent distortion energy of Mo\(_{(1-x)}\)W\(_x\)S\(_2\) for each atom can be obtained. Also, we get the interaction parameter of \(\Omega = 1.027\) eV (see Figure 4a). In addition, Figure 4b−d show the pressure-dependent energy change of single M−S bond in Mo\(_{(1-x)}\)W\(_x\)S\(_2\) including bond stretching, bond angle variation, and electrostatic interaction with the composition at \(x = 0, 0.25, 0.5, 0.75,\) and 1, respectively. Obviously, the energy from bond stretching and bond angle relaxation is monotonically decreasing, and the electrostatic interaction increases approximately linearly with increasing pressure. Figure 4e depicts that the interlayer interaction of an S atom decreases approximately linearly with increasing pressure in terms of eq 4. According to the ABR consideration,\textsuperscript{50−52} external perturbation such as doping and pressure can lead to the system relaxing spontaneously to a new self-equilibrium state. Therefore, some physical quantities such as cohesive energy will be different from that of the bulk counterparts.
Theoretically, the cohesive energy is defined as:
$$E_C = z_n E_n,$$
and the cohesive energies of monolayer MoS$_2$ and WS$_2$ are 1.35 and 2.15 eV, respectively.$^{49}$ For the case of Mo$_{(1-x)}$W$_x$S$_2$, the average single bond energy can be expressed as the function of composition, number of layers, and hydrostatic pressure, that is,
$$E_b(x, p, n) = (1-x)E_n^A + xE_n^B + \Delta E.$$  
In Figure 4f, we can see that the single bond energy in the bulk Mo$_{(1-x)}$W$_x$S$_2$ immediately decreases with applied pressure due to the strong interlayer interactions. Whereas in the case of bilayer and monolayer, the single bond energy in a small pressure range increases initially. Interestingly, it will intersect with the composition at $0 < x < 0.46$ due to the existence of distortion energy.  

Furthermore, Figure 5 depicts the bandgap of MoS$_2$, Mo$_0.5$W$_0.5$S$_2$, and WS$_2$ as a function of pressure under the condition of monolayer, bilayer, and bulk, respectively. Evidently, the bandgaps of MoS$_2$, Mo$_0.5$W$_0.5$S$_2$, and WS$_2$ in bulk counterparts decrease with increasing pressure. For the cases of bilayer and monolayer, the bandgaps increase initially and then gradually decrease with increasing pressure. In detail, in Figure 5a, we can see that the extreme points at 19.2, 21.1, and 24.3 GPa correspond to the bandgaps of 2.08, 2.21, and 2.47 eV for the monolayer MoS$_2$, Mo$_0.5$W$_0.5$S$_2$, and WS$_2$, and the metallization at pressures of 68.8, 76.2, and 81.5 GPa, whereas the extreme points for the bilayer at 4.3, 6.9, and 10.8 GPa indicate the bandgaps of 1.58, 1.61, and 1.89 eV. Also, the metallization for the bilayer is at pressures of 38.4, 41.5, and 43.7 GPa, respectively. Furthermore, the metallization of bulk MoS$_2$, Mo$_0.5$W$_0.5$S$_2$, and WS$_2$ at pressures of 23, 27, and 30 GPa, respectively. Importantly, there will be the intersection between the bandgaps with the composition $x < 0.46$ by the range of pressure less than 5 GPa. Interestingly, higher W composition in monolayer Mo$_{(1-x)}$W$_x$S$_2$ contributes to a greater pressure-sensitivity of direct bandgap opening. In addition, Figure 5b shows the bandgap of monolayer Mo$_{(1-x)}$W$_x$S$_2$ as a function of pressure in the small pressure range. Obviously, a near-linear enhancement of the bandgap is shown below 6 GPa, whereas its increment slows down above 6 GPa. Importantly, our
predictions are consistent with the previous works. In fact, the conduction band minimum (CBM) and the valence band maximum (VBM) are dominated by d orbitals of metal elements and the p orbitals of S atoms. For the case of monolayer Mo$_{1-x}$W$_x$S$_2$, the orbitals move away the Fermi level at lower pressure, resulting in the bandgap increasing as the pressure enhances, whereas the rising rate increases with increasing W composition. At higher pressure, the orbitals interact strongly between M d and S p, resulting in the decrease of bandgap and finally there is an overlap of VBM and CBM. Importantly, there has been a direct-to-indirect transition, while the intralayer interaction of in-plane plays a dominant role for the process of metallization. Similarly, the trend of bandgap in bilayer Mo$_{1-x}$W$_x$S$_2$ is consistent with the change of monolayer under pressure, but the magnitude of the change is somewhat different because of the limitation of interactions between layers. In the case of bulk Mo$_{1-x}$W$_x$S$_2$, the VBM and CBM are close to the Fermi level with applied pressure because of the limit of sulfur-sulfur interactions, resulting in the decrease of bandgap and finally metallization. Moreover, the metallization pressure increases when the W composition enhances.

Based on the discussion mentioned above, we further explored the pressure, composition, and layer number dependence of semiconductor-to-metal transition in Mo$_{(1-x)}$W$_x$S$_2$, as shown in the Figure 6. In detail, the solid line represents the transition point. Clearly, it can be concluded that the transition from semiconductor-to-metal is more easy with increasing number of layers. When the layer number is fixed, the transition pressure increases with increasing W composition. Similarly, Nayak et al. indicated that as the number of layers increase, the transition pressure of semiconductor-to-metal in MoS$_2$ decreases. Kim et al. also showed that the transition pressure of semiconductor-to-metal increase with increasing number of layers, whereas lower W composition results in a delayed semiconductor-to-metal transition in Mo$_{(1-x)}$W$_x$S$_2$. Importantly, the physical origin of transition for the monolayer Mo$_{(1-x)}$W$_x$S$_2$ can be attributed to the change of M–S bond length under pressure because of the absence of interlayer interactions. For the bilayer and bulk alloys of Mo$_{(1-x)}$W$_x$S$_2$, the compression of interlayer becomes more favorable than that of intralayer, indicating that the interlayer coupling of S–S increases at the pressure, resulting in the transition of semiconductor-to-metal, and the metal-

Figure 4. (a) Distortion energy of each atom varies with composition in Mo$_{(1-x)}$W$_x$S$_2$, (b) pressure-dependent single M–S bond energy at $x = 0$, 0.25, 0.5, 0.75, and 1, (c) bond stretching and bond angle energies, (d) electrostatic interactions, (e) interlayer interactions of an S atom, and (f) change of average single bond energy for the monolayer, bilayer, and bulk Mo$_{(1-x)}$W$_x$S$_2$ as a function of pressure, respectively.
In summary, we propose a quantitative approach to investigate the relaxation of bond identities, band offset, and semiconductor-to-metal transition in \( \text{Mo}_{1-x}\text{W}_x\text{S}_2 \) with different number of layers under hydrostatic pressure in terms of ABR correlation mechanism. It was found that the bulk modulus of monolayer \( \text{Mo}_{1-x}\text{W}_x\text{S}_2 \) is significantly larger than that of its bilayer and bulk counterparts due to the lack of interlayer interaction, and the bulk modulus of bilayer is slightly larger than that of bulk because the bulk modulus is mainly controlled by interlayer interactions, whereas the bulk modulus increases slightly with increasing composition. In nature, the variations of bond identities change the total energy of the entire system. Thus, the bandgaps of monolayer and bilayer show a blue-shift and then red-shift with increasing pressure, whereas the bandgap of bulk \( \text{Mo}_{1-x}\text{W}_x\text{S}_2 \) displays a red-shift with increasing pressure owing to the strong coupling of interlayer. Moreover, the transition of semiconductor-to-metal decreases with increasing layer number in the \( \text{Mo}_{1-x}\text{W}_x\text{S}_2 \) under pressure approach. Also, the transition pressure increases with increasing W composition when the layer number is fixed. Our predictions are in good agreement with the available experimental observations and calculations, suggesting that the method can be suitable for the layered materials for the desired applications.

4. CONCLUSIONS

Corresponding Author
*E-mail: ganguouy@hunnu.edu.cn.

ORCID
Gang Ouyang: 0000-0003-2589-9641

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (grant nos. 11574080 and 91833302).

REFERENCES

(1) Wang, Q. H.; Kalantar-Zadeh, K.; Kis, A.; Coleman, J. N.; Strano, M. S. Electronics and Optoelectronics of Two-Dimensional Transition Metal Dichalcogenides. Nat. Nanotechnol. 2012, 7, 699–712.
(2) Jariwala, 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.
(3) Fiori, G.; Bonaccorso, F.; Iannaccone, G.; Palacios, T.; Neumaier, D.; Seabaugh, A.; Banerjee, S. K.; Colombo, L.; Colombo, L. Electronics based on Two-Dimensional Materials. Nat. Nanotechnol. 2014, 9, 768–779.
(4) Wu, W.; Wang, L.; Li, Y.; Zhang, F.; Lin, L.; Niu, S.; Chenet, D.; Zhang, X.; Hao, Y.; Heinz, T. F.; Hone, J.; Wang, Z. L. Piezoelectricity of single-atomic-layer MoS\(_2\) for energy conversion and piezotronics. Nature 2014, 514, 470.
(5) Manzeli, S.; Ovchinnikov, D.; Pasquier, D.; Yazyev, O. V.; Kis, A. 2D Transition Metal Dichalcogenides. Nat. Rev. Mater. 2017, 2, 17033.
(6) Zhou, J.; Lin, J.; Huang, X.; Zhou, Y.; Chen, Y.; Xia, J.; Wang, H.; Xie, Y.; Yu, H.; Lei, J.; Wu, L.; Liu, F.; Fu, Q.; Zeng, Q.; Hsu, C.-H.; Yang, C.; Lu, L.; Yu, T.; Shen, Z.; Lin, H.; Yakobson, B. I.; Liu, Q.; Suenaga, K.; Liu, G.; Liu, Z. A Library of Atomically Thin Metal Chalcogenides. Nature 2018, 556, 355.
(7) Liu, X.; Hu, J.; Yue, C.; Della Fera, N.; Ling, Y.; Mao, Z.; Wei, J. High Performance Field-Effect Transistor based on Multilayer Tungsten Disulfide. ACS Nano 2014, 8, 10396–10402.

(8) Mak, K. F.; Lee, C. G.; Hone, J.; Shan, J.; Tony, F.; Heinz, T. F. Atomically Thin MoS2: A New Direct-Gap Semiconductor. Phys. Rev. Lett. 2010, 105, 136805.

(9) Kuc, A.; Zibouche, N.; Heine, T. Influence of Quantum Confinement on The Electronic Structure of The Transition Metal Sulfide TSS2. Phys. Rev. B: Condens. Matter Mater. Phys. 2011, 83, 245213.

(10) Drummond, C.; Alcantar, N.; Israelachvili, J.; Tenne, R.; Golan, Y. Microtribology and Friction-Induced Material Transfer in WS2 Nanoparticle Additives. Adv. Funct. Mater. 2001, 11, 348.

(11) 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.

(12) Song, J.-G.; Ryu, G. H.; Lee, S. J.; Sim, S.; Lee, C. W.; Choi, T.; Jung, H.; Kim, Y.; Lee, Z.; Myoung, J.-M.; Dussarrat, C.; Lansalot-Matras, C.; Park, J.; Choi, H.; Kim, H. Controllable Synthesis of Molybdenum Tungsten Disulfide Alloy for Vertically Composition-Controlled Multilayer. Nat. Commun. 2015, 6, 7817.

(13) Dolui, K.; Pemmavaraju, C. D.; Sanvito, S. Electric Field Effects on Armchair MoS2 Nanoribbons. ACS Nano 2012, 6, 4823–4834.

(14) Chen, Y.; Xi, J.; Duncencmo, D. O.; Liu, Z.; Suenaga, K.; Wang, D.; Shuai, Z.; Huang, Y.-S.; Xie, L. Tunable Band Gap Photoluminescence From Atomically Thin Transition-Metal Dichalcogenide Alloys. ACS Nano 2013, 7, 4610–4616.

(15) Park, J.; Kim, M. S.; Park, B.; Oh, S. H.; Roy, S.; Kim, J.; Choi, W. Composition-Tunable Synthesis of Large-Scale Mo1-xWxS2 Alloys with Enhanced Photoluminescence. ACS Nano 2018, 12, 6301–6309.

(16) Komsa, H.-P.; Krasheninnikov, A. V. Two-dimensional Transition Metal Dichalcogenide Alloys: Stability and Electronic Properties. J. Phys. Chem. Lett. 2012, 3, 3652–3656.

(17) Tan, T. L.; Ng, M.-F.; Eda, G. Stable Monolayer Translation Metal Dichalcogenide Ordered Alloys With Tunable Electronic Properties. J. Phys. Chem. C 2016, 120, 2501–2508.

(18) Pandey, M.; Jacobsen, K. W.; Thyzesen, K. S. Atomically Thin Ordered Alloys of Transition Metal Dichalcogenides: Stabilities and Band Structures. J. Phys. Chem. C 2016, 120, 23024–23029.

(19) Aksoy, R.; Ma, Y.; Selvi, E.; Chyu, M. C.; Ertas, A.; White, A. X-ray diffraction study of molybdenum disulfide to 38.8GPa. J. Phys. Chem. Solids 2006, 67, 1914–1917.

(20) Selvi, E.; Ma, Y.; Aksoy, R.; Ertas, A.; White, A. High Pressure X-ray Diffraction Study of Tungsten Disulfide. J. Phys. Chem. Solids 2006, 67, 2183–2186.

(21) Nayak, A. P.; Bhattacharyya, S.; Zhu, J.; Liu, J.; Wu, X.; Pandey, T.; Jin, C.; Singh, A. K.; Akinwande, D.; Lin, J. F. Pressure-Induced Semiconduction to Metallic Transition in Multilayered Molybdenum Disulphide. Nat. Commun. 2014, 5, 4731.

(22) Hromadova, L.; Marton, R.; Tosatti, E. Structure Change, Layer Sliding, and Metalization in High-Pressure MoS2. Phys. Rev. B: Condens. Matter Mater. Phys. 2013, 87, 144105.

(23) Bandaru, N.; Kumar, R. S.; Sneyd, D.; Tschauker, O.; Baker, J.; Antonio, D.; Luo, S.-N.; Hartmann, T.; Zhao, Y.; Venkat, R. Effect of Pressure and Temperature on Structural Stability of MoS2. J. Phys. Chem. C 2014, 118, 3230–3235.

(24) Chi, Z.-H.; Zhao, X.-M.; Zhang, H.; Goncharov, A. G.; Lobanov, S. S.; Kagayama, T.; Sakata, M.; Chen, X.-J. Pressure-Induced Metalization of Molybdenum Disulfide. Phys. Rev. Lett. 2014, 113, 036802.

(25) O’Neal, K. R.; Cherian, J. G.; Zak, A.; Tenne, R.; Liu, Z.; Musfeldt, J. L. High Pressure Vibrational Properties of WS2 Nanotubes. Nano Lett. 2016, 16, 993–999.

(26) Guo, H.; Yang, T.; Tao, P.; Wang, Y.; Zhang, Z. High Pressure Effect on Structure, Electronic Structure, and Thermoelectric Properties of MoS2. J. Appl. Phys. 2013, 113, 013709.

(27) Fan, X.; Chang, C.-H.; Zheng, W. T.; Kuo, J.-L.; Singh, D. J. The Electronic Properties of Single-layer and Multilayer MoS2 Under High Pressure. J. Phys. Chem. C 2015, 119, 10189–10196.

(28) Ouyang, G.; Yang, G.; Sun, C.; Zhu, W. Nanoporous Structures: Smaller is Stronger. Small 2008, 4, 1359–1362.

(29) Ouyang, G.; Zhu, W. G.; Sun, C. Q.; Zhu, Z. M.; Liao, S. Z. Atomic Origin of Lattice Strain on Stiffness of Nanoparticles. Phys. Chem. Chem. Phys. 2010, 12, 1543–1549.

(30) Dou, X.; Ding, K.; Jiang, D.; Sun, B. Tuning and Identification of Interband Transitions in Monolayer and Bilayer Molybdenum Disulfide Using Hydrostatic Pressure. ACS Nano 2014, 8, 7458–7464.

(31) Nayak, A. P.; Pandey, T.; Voiry, D.; Liu, J.; Moran, S. T.; Sharma, A.; Tan, C.; Chen, C.-H.; Li, L.-J.; Chihowalla, M.; Lin, J.-F.; Singh, A. K.; Akinwande, D. Pressure-Dependent Optical and Vibrational Properties of Monolayer Molybdenum Disulfide. Nano Lett. 2014, 15, 346–353.

(32) Li, F.; Yan, Y.; Han, B.; Li, L.; Huang, X.; Yao, M.; Gong, Y.; Jin, X.; Liu, B.; Zhu, C.; Zhou, Q.; Cui, T. Pressure Confinement Effect in MoS2 Monolayers monolayers. Nanoscale 2015, 7, 9075–9082.

(33) Dou, X.; Ding, K.; Jiang, D.; Fan, X.; Sun, B. Probing Spin-Orbit Coupling and Interlayer Coupling in Atomically Thin Molybdenum Disulfide Using Hydrostatic Pressure. ACS Nano 2016, 10, 1619–1624.

(34) Kim, J.-S.; Ahmad, R.; Pandey, T.; Rai, A.; Feng, S.; Yang, J.; Lin, Z.; Terrones, M.; Banerjee, S. K.; Singh, A. K.; Akinwande, D.; Lin, J.-F. Towards Band Structure and Band Offset Engineering of Monolayer Mo1-xWxS2 Via Strain. 2D Mater. 2017, 5, 015008.

(35) Suzuki, S.; Kawamura, M. Study of Vibrational Spectra of Interlayer Water in Sodium Beidellite by Molecular Dynamics Simulations. J. Phys. Chem. B 2004, 108, 13468–13474.

(36) Onodera, T.; Morita, Y.; Suzuki, A.; Koyama, M.; Tsuboi, H.; Hatakeyama, N.; Endou, A.; Takaha, H.; Kubo, M.; Dassenoy, F.; Minfray, C.; Joly-Pottuz, L.; Martin, J.-M.; Miyamoto, A. A Computational Chemistry Study on Friction of h-MoS2. Part I. Mechanism of Single Sheet Lubrication. J. Phys. Chem. B 2009, 113, 16526–16536.

(37) Xiong, S.; Cao, G. Molecular Dynamics Simulations of Mechanical Properties of Monolayer MoS2. Nanotechnology 2015, 26, 185705.
(47) Liang, T.; Phillpot, S. R.; Sinnott, S. B. Parametrization of A Reactive Many-Body Potential for Mo-S Systems. Phys. Rev. B: Condens. Matter Mater. Phys. 2009, 79, 245110.

(48) Nicolini, P.; Polcar, T. A Comparison of Empirical Potentials for Sliding Simulations of MoS₂. Comput. Mater. Sci. 2016, 115, 158–169.

(49) Liu, Y.; Wang, Y.; Bo, M.; Liu, X.; Yang, X.; Huang, Y.; Sun, C. Q. Thermally Driven (Mo, W)-(S₂, Se₂) Phonon and Photon Energy Relaxation Dynamics. J. Phys. Chem. C 2015, 119, 25071–25076.

(50) Sun, C. Q. Size Dependence of Nanostructures: Impact of Bond Order Deficiency. Prog. Solid State Chem. 2007, 35, 1–159.

(51) Ouyang, G.; Wang, C. X.; Yang, G. W. Surface Energy of Nanostructural Materials with Negative Curvature and Related Size Effects. Chem. Rev. 2009, 109, 4221–4247.

(52) Zhang, A.; Zhu, Z.; He, Y.; Ouyang, G. Structure Stabilities and Transitions in Polyhedral Metal Nanocrystals: An Atomic-Bond-Relaxation Approach. Appl. Phys. Lett. 2012, 100, 171912.

(53) Zhu, Z.; Zhang, A.; Ouyang, G.; Yang, G. Edge Effect on Band Gap Shift in Si Nanowires with Polygonal Cross-Sections. Appl. Phys. Lett. 2011, 98, 263112.

(54) Chang, C.-H.; Fan, X.; Lin, S. H.; Kuo, J. L. Orbital Analysis of Electronic Structure and Phonon Dispersion in MoS₂, MoSe₂, WS₂, and WSe₂ Monolayers Under Strain. Phys. Rev. B: Condens. Matter Mater. Phys. 2013, 88, 195420.

(55) Li, T. Ideal Strength and Phonon Instability in Single-Layer MoS₂. Phys. Rev. B: Condens. Matter Mater. Phys. 2012, 85, 235407.

(56) Ghorbani-Ad, M.; Borini, S.; Kuc, A.; Heine, T. Strain-Dependent Modulation of Conductivity in Single-Layer Transition-Metal Dichalcogenides. Phys. Rev. B: Condens. Matter Mater. Phys. 2013, 87, 235434.

(57) Aitken, Z. H.; Huang, R. Effects of Mismatch Strain and Substrate Surface Corrugation on Morphology of Supported Monolayer Graphene. J. Appl. Phys. 2010, 107, 123531.

(58) Cooper, R. C.; Lee, C.; Marianetti, C. A.; Wei, X. D.; Hone, J.; Kysar, J. W. Nonlinear Elastic Behavior of Two-Dimensional Molybdenum Disulfide. Phys. Rev. B: Condens. Matter Mater. Phys. 2013, 87, 035423.

(59) Liu, K.; Yan, Q.; Chen, M.; Fan, W.; Sun, Y.; Suh, J.; Fu, D.; Lee, S.; Zhou, J.; Tongay, S.; Ji, J.; Neaton, J. B.; Wu, J. Elastic Properties of Chemical-Vapor-Deposited Monolayer MoS₂, WS₂, and Their Bilayer Heterostructures. Nano Lett. 2014, 14, 5097–5103.

(60) Birch, F. Finite Elastic Strain of Cubic Crystals. Phys. Rev. 1947, 71, 809.

(61) Ouyang, G.; Sun, C. Q.; Zhu, W.-G. Pressure-Stiffened Raman Phonons in Group III Nitrides: A Local Bond Average Approach. J. Phys. Chem. B 2008, 112, 5027–5031.

(62) Li, C.; Wu, P. Correlation of Bulk Modulus and The Constituent Element Properties of Binary Intermetallic Compounds. Chem. Mater. 2001, 13, 4642–4648.