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Density functional studies on edge-contacted single-layer MoS_2 piezotronic transistors

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The piezotronic effect uses strain-induced piezoelectric charges at interfaces and junctions to tune and/or control carrier transport in piezoelectric semiconductor devices. This effect has recently been observed in single-layer 2D MoS_2 materials. However, previous work had found that metallic states are generated at the edge of a free-standing MoS_2 flat sheet, and these states may screen the piezoelectric charges. Using density functional theory simulations, we found that the metal–MoS_2 interface structure plays an important role in enhancing both the piezoelectric and piezotronic effects in MoS_2 transistors by breaking the metallic state screening effect at the MoS_2 edge. This study not only provides an understanding of the piezoelectric and piezotronic effects based on first principles calculations but also offers guidance for the design of two-dimensional piezotronic devices. © *2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4929726]

Piezoelectric semiconductors, such as wurtzite-structured ZnO, GaN, and InN, have coupled piezoelectric and semiconductor properties that can be used to fabricate functional electronics.[1] Piezoelectric charges created at an interface or junction by externally applied strain can tune or control electronic transport characteristics, and this is referred to as the piezotronic effect.[2] The piezotronic effect has been used to design and fabricate unique electromechanical functional devices such as nanogenerators,[1] logic devices,[3] flexible human-machine interfaces,[4] and photonic-strain sensor arrays.[5]

Recently, piezoelectric and piezotronic effects have been observed not only in one-dimensional (1D) wurtzite piezoelectric semiconductor nanowires, such as ZnO, GaN, InN, and CdS,[2] but also have been observed in two-dimensional (2D) single-atomic-layer MoS_2.[6] Previous theoretical studies have predicted the possible piezoelectricity of an infinite periodic single MoS_2 layer based on first principles simulations,[7] but scanning tunneling microscopy (STM) and density functional theory (DFT) simulation studies found that a finite free-standing MoS_2 flat sheet was enclosed by edge-localized metallic states,[8,9] which can have a screening effect and prevent the piezoelectric output. Therefore, observation of the piezoelectric effect in MoS_2 [6] raises important questions as to how the metallic state screening effect can be broken in MoS_2 and why piezoelectric and piezotronic effects can be observed at MoS_2–metal interfaces.

In this letter, the piezoelectric polarization, the piezo-charge distribution, and the Schottky barrier height are calculated using DFT by comparing single-layer MoS_2 transistors with the free-standing MoS_2 flat sheet model. The metal–MoS_2 interface structure plays an essential role, enhancing the piezoelectric effect by breaking the metallic state screening effect at the MoS_2 edge, and thus piezoelectric charges change the Schottky barrier height and tune or control the carrier transport, which is essentially the piezotronic effect in single-layer MoS_2 transistors. Without the metal–MoS_2 interface structure, a finite free-standing MoS_2 flat sheet shows the metallic states at the MoS_2 edge that screen the piezoelectric effect. This study provides an understanding of the piezoelectric and piezotronic effects in 2D materials and guidance for future design of 2D piezotronic transistors.

According to previous experimental and theoretical studies,[6,8] three typical metal–MoS_2 interface structures are used to model metal–MoS_2–metal transistors: metal–sulfur, metal–molybdenum, and metal–excess sulfur structures.[8] Pd is selected as the electrode metal in this study.[6] Figure 1 shows three typical transistor models with the corresponding metal–MoS_2 edge interface structures. The stoichiometry transistor (*Sch-transistor*) (Fig. 1(a)) was used in an experiment[6] in which the numbers of Mo and S atoms had a ratio of 1:2; the $(\bar{1}010)$ edge of the MoS_2 is terminated by the S atoms and the $(10\bar{1}0)$ edge is terminated by the Mo atoms. The excess-S transistor (*ExS-transistor*) (Fig. 1(b))[8] has the $(10\bar{1}0)$ edge of the MoS_2 layer saturated with excess S atoms. The reverse transistor (*Rv-transistor*) (Fig. 1(c)) is our structure, where the $(\bar{1}010)$ edge is terminated by Mo atoms and the $(10\bar{1}0)$ edge is terminated by S atoms, and is thus a reverse case of the Sch-transistor. Using these three structures, we simulate the effects of different MoS_2 edge geometries on the piezoelectric and piezotronic effects. In the Sch- and Rv-transistors, 12 single columns of Mo–S atoms are included along the z-axis, while in the ExS-transistor, an additional column of S atoms is included at the $(10\bar{1}0)$ edge of MoS_2. In our model, a simple orthorhombic supercell is adopted. The Pd[111] direction is parallel to the z-axis, and the MoS_2 layer is parallel to the x-z plane. The zigzag edge of the MoS_2 layer is in direct contact with the

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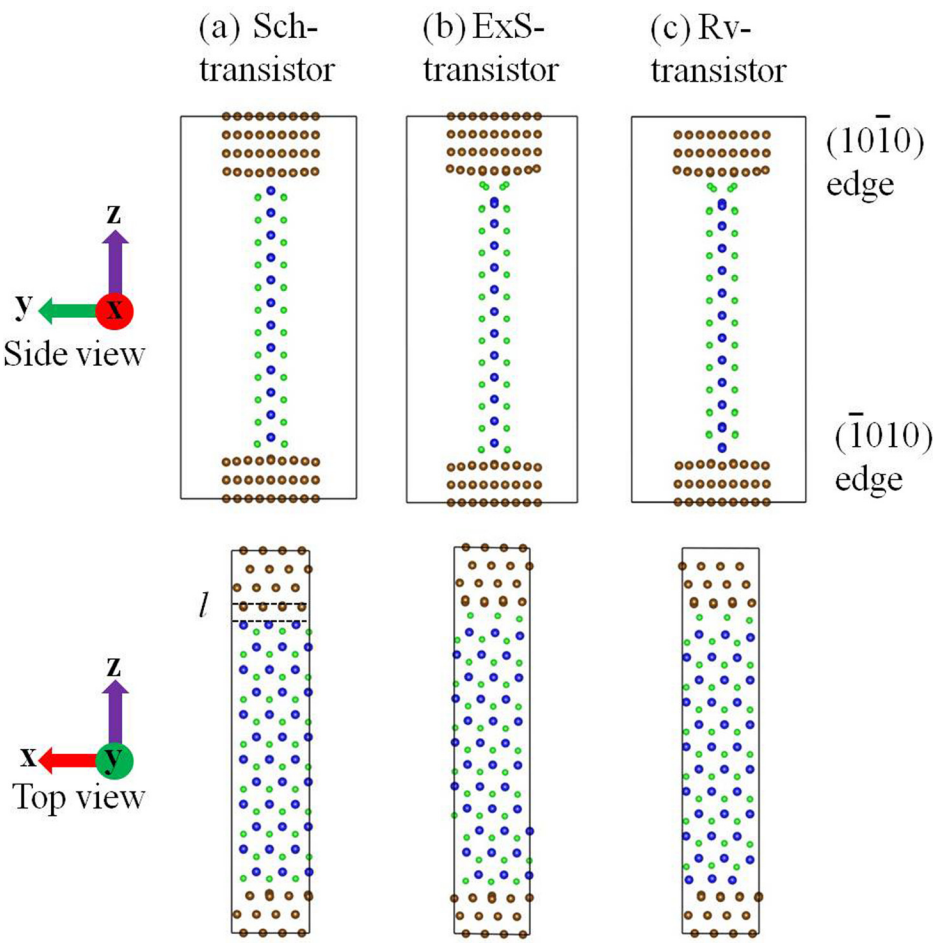

FIG. 1. Three different transistors used in the present calculations: (a) stoichiometry transistor (Sch-transistor), (b) excess-S transistor (ExS-transistor), and (c) reverse transistor (Rv-transistor). Each transistor has a different metal–MoS_2 contact geometry. In the figure, the blue balls indicate Mo atoms, the green balls indicate S atoms, and brown balls indicate Pd atoms.

Pd(111) plane, which is strained 2% to eliminate the lattice mismatch with MoS_2. According to previous calculation, a 2% strain on the metal electrode does not cause obvious changes to the electronic structure or to the Schottky barrier at the metal-semiconductor interface.[10,11] Periodic boundary conditions are applied to the x, y, and z directions of the supercell. To avoid the interactions between neighboring MoS_2 layers along the y direction, a vacuum layer with width of 11 Å is added to the supercell, which is larger than the value adopted in a previous theoretical study.[8] A convergence test on the calculation results indicates that the adopted vacuum layer width is sufficient. To obtain relaxed equilibrium transistor structures with minimum strain and the lowest possible energy, an optimal contact distance between the MoS_2 and the Pd electrode (referred to as l in Fig. 1) is obtained without relaxing any other structural parameters; then, the cell constants and the atomic positions, including all MoS_2 atoms and the Pd layers closest to MoS_2, are fully relaxed to eliminate the strain. The Pd atoms in the inner electrode hardly change their positions during the structural relaxation, so they are regarded as being fixed to reduce the number of calculations. An external strain (ranging from −5% to 5%) is applied along the z-axis by compressing and/or stretching the cell constant of the equilibrium transistor while keeping the fractional coordinates of all atoms fixed. Then, all MoS_2 atoms and interface Pd layer atoms are fully relaxed by fixing the cell constants. For comparison with the transistors, single-layer free-standing MoS_2 flat sheets, including the Sch-flat sheet, the ExS-flat sheet, and the Rv-flat sheet, are also constructed by deleting all Pd atoms from the corresponding transistor models.[8] In previous experiment,[12] an in-plane tensile strain can reach to 11% and results in a 4% compressive strain in the transverse direction in the MoS_2 plane (the Poisson ration of the single-layer MoS_2 is 0.34 according to Ref. 7). Thus, strains (ranging from −5% to 5%) are adopted in this study.

The transistor simulations are based on DFT using the Vienna *ab initio* simulation package (VASP)[13,14] with frozen-core projector-augmented-wave (PAW) pseudopotentials.[15,16] The exchange correlation potentials are treated by Perdew–Burke–Ernzerhof (PBE) parameterization within the general gradient approximation (GGA).[17] A k-point sampling of a $3 \times 1 \times 1$ mesh is used in the structural optimization, and a $9 \times 1 \times 1$ mesh is used for the properties calculations. A plane-wave energy cutoff of 400 eV is used when calculating the energy and electron densities.[10]

According to piezotronic theory, when an external strain is applied to a metal–semiconductor–metal (MSM) transistor structure, piezocharges with opposite signs are created at the two Pd–MoS_2 interfaces, which can then tune and control the electronic transport characteristics. The strain-dependent piezoelectric polarization along the z-axis of the transistor can be obtained through DFT calculations.[18] Larger changes in the polarization of the transistor under applied strain reflect a stronger piezotronic effect. From the definition of dipole moments,[18] the polarization can be obtained directly: the dipole moment of the transistor along the z-axis is obtained by adding the dipole moments of the positive ionic

charges and the negative electronic charges within the transistor cell, and then the polarization of the 2D transistor is obtained by dividing the dipole by the cell area in the x-z plane.[18] Figure 2 shows the polarizations of the Sch-, ExS-, and Rv-transistors under externally applied strains, using the polarizations of the corresponding transistors under zero strain as reference values. The polarizations of the transistors with the different Pd–MoS_2 interface geometries are similar to each other under the applied strains. From these polarizations, the piezoelectric constants of the three transistors can be obtained; they are $2.46 \times 10^{-10}\,Cm^{-1}$ for the Sch-transistor, $2.61 \times 10^{-10}\,Cm^{-1}$ for the ExS-transistor, and $2.54 \times 10^{-10}\,Cm^{-1}$ for the Rv-transistor, and they are all close to the recently experimentally measured value[19] of $2.9 \times 10^{-10}\,Cm^{-1}$ and the previously calculated value[7] of $3.64 \times 10^{-10}\,Cm^{-1}$. Our results show that the piezoelectric polarization, and thus the piezotronic effect of the MoS_2 transistor, is an intrinsic property of the single MoS_2 layer and is independent of the interface structures. The stability of the piezotronic effect among the interface structures is beneficial for device applications to MoS_2 transistors. In contrast, all the free-standing MoS_2 flat sheet structures show zero polarizations under externally applied strains, as shown in Fig. 2, because the edge metallic states around the single-layer MoS_2 flat sheet screen the piezoelectric charges, as demonstrated in previous experimental and theoretical studies.[8] The above result shows that the Pd–MoS_2 interface plays an essential role in preserving the piezoelectric polarization, and thus enhances the piezotronic effect in MoS_2 transistors.

The mechanism by which the piezotronic effect is enhanced by the metal–MoS_2 interface structure can be understood from the electronic structures. Taking the equilibrium Sch-transistor and the Sch-sheet as an example, the local density of states (LDOS) of the Mo and S atoms in these two structures are calculated using DFT, as shown in Fig. 3. The MoS_2 in the Sch-sheet shows strong metallic behavior because a number of states are located at the Fermi level, as shown in Fig. 3(a). These metallic states can be attributed to the atoms near the two edges: Fig. 3(b) gives the LDOS of single-column Mo–S atoms at the $(\bar{1}010)$ edge, in which a large peak appears at the Fermi level. The p electrons of the S atoms make a dominant contribution in the peak; the LDOS of the single-column Mo–S atoms at the $(10\bar{1}0)$ edge is shown in Fig. 3(c). Similar to the case at the $(\bar{1}010)$ edge, a peak also appears at the Fermi level, which is mainly formed because of the d electrons of the Mo atoms. These p and d electrons become unbounded free electrons at the two edges of a free-standing MoS_2 flat sheet and screen the piezocharge, thus leading to the zero piezoelectric polarization of the Sch-flat sheet in Fig. 2. In the Sch-transistor, however, by connecting the edge Mo and S atoms to the Pd electrodes, the total LDOS of MoS_2 in the transistor decreases at the Fermi level, as shown in Fig. 3(a). From Figs. 3(b) and 3(c), the reduction in the number of metallic states is due to saturation of the S atoms at the $(\bar{1}010)$ edge and the Mo atoms at the $(10\bar{1}0)$ edge by the Pd electrode. The bonding of the p electrons of the S atoms and the d electrons of the Mo atoms reduces the number of unbounded electrons and thus prevents the screening effect of the metallic electrons, leading to the obvious piezoelectric polarization of the Sch-transistor in Fig. 2. For the single-column Mo–S structures in the inner MoS_2, either in the transistor structure or in the free-standing flat sheet, the LDOS values in Fig. 3(d) show that they are semiconductive, which is the same as for the infinitely large single-layer MoS_2.[8] The analysis above is also valid for the ExS- and Rv-transistors and the free-standing MoS_2 flat sheets.

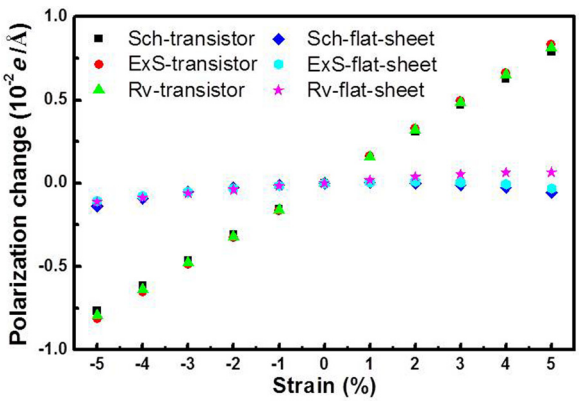

FIG. 2. Polarizations of the Sch-, ExS-, and Rv-transistors under strain, using their equilibrium structures for reference values. For comparison, the polarizations of the corresponding free-standing MoS_2 sheets are also shown in the figure. e is the absolute electron charge, where $e = 1.6 \times 10^{-19}$ C.

From the calculated piezoelectric polarizations and the LDOS shown above, we can explain our previous experimental and theoretical results with regard to the piezoelectricity of single-layer MoS_2 as follows: the infinitely large periodic single-layer MoS_2 is both semiconductive and piezoelectric because of its non-centrosymmetric structure;[7] however, finite free-standing MoS_2 flat sheets do not show piezoelectricity because of the existence of enclosed metallic states at the edge that screen the piezocharges; in the MoS_2 transistor, by contacting the free-standing MoS_2 flat sheet with a metal electrode, the metallic states are diminished because of the bonding between the metal and the edge Mo/S atoms at the interfaces, which suppresses the screening effects of the metallic electrons and leads to strong piezoelectric and piezotronic effects. This explanation agrees well with previous experimental and theoretical results and provides a means of enhancing the piezotronic effect in 2D materials.

Piezoelectric and piezotronic effects are both intrinsic properties of a single MoS_2 layer. To understand these intrinsic properties, we calculate the piezocharge distributions and Schottky barrier heights at the metal–MoS_2 interface under external applied strain using the method from our previous theoretical work.[20] Taking the Sch-transistor as an example, the piezocharge densities are calculated as follows. (1) The planar averaged electrostatic potential and charge density of the transistor along the z-axis are obtained. (2) The inner MoS_2 and Pd regions and the interface regions in the transistor are selected. The inner Pd region has a width equal to the layer distance between the Pd(111) planes, the inner MoS_2 region has a width equal to the distance between neighboring Mo or S layers, and the interface region has the minimum width while ensuring that the total charge of the inner Pd and MoS_2 regions is zero. (3) According to classical piezotronic

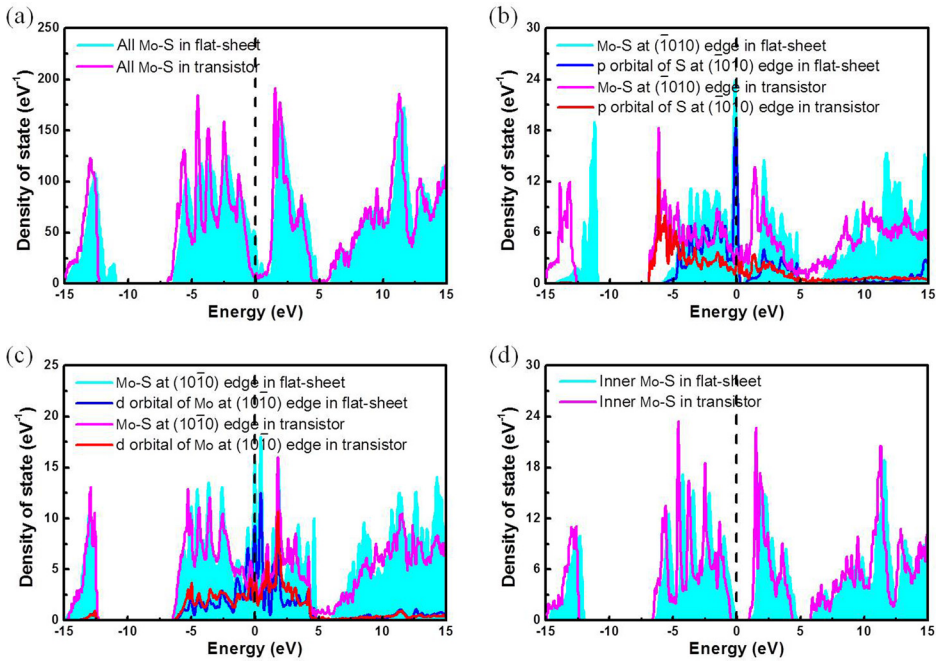

FIG. 3. Local density of states (LDOS) of (a) all Mo and S atoms in an equilibrium Sch-transistor or a free-standing MoS_2 sheet; (b) single-column Mo–S atoms at the $(\bar{1}010)$ edge in the Sch-transistor or in a free-standing MoS_2 sheet (the LDOS of the p orbital of the edge S atoms is also included); (c) single-column Mo–S atoms at the $(10\bar{1}0)$ edge (the LDOS of the d orbital of the edge Mo atoms is also included); and (d) single-column Mo–S atoms at the inner part of a transistor or a free-standing MoS_2 sheet.

theory, the piezocharges that are distributed at the interface are calculated as the charge density difference between the transistor in equilibrium and another transistor under strain. The Schottky barrier modulations at the metal–semiconductor interfaces due to the piezotronic effect are calculated as changes in the reference potential at the interfaces.[11,20] The piezocharge distribution of the Sch-sheet is calculated in the same interface region as that of the Sch-transistor. Figures 4(a) and 4(b) show the piezocharge distributions of the Sch-transistor and a corresponding free-standing MoS_2 sheet at the $(\bar{1}010)$ and $(10\bar{1}0)$ interfaces/surfaces, respectively. Figure 4(c) shows the total number of piezocharges per transistor/sheet width for the Sch-, ExS-, and Rv-transistors and the flat sheets versus applied strain at the $(\bar{1}010)$ interface/surface, and Fig. 4(d) shows the modulation of the Schottky barrier height under strain at the $(\bar{1}010)$ interface for the Sch-, ExS- and Rv-transistors. These results are in accordance with both classical piezotronic theory and the results of the previous experiment.[6] Note that the total number of piezocharges in the transistors is almost the same in magnitude as that in the corresponding free-standing MoS_2 sheets, indicating that the piezoelectric and piezotronic effects are intrinsic properties of a single MoS_2 layer. However, as we have mentioned previously, the Pd electrode is significant in that it changes the electronic properties of the electrons at the MoS_2 edge. Figures 4(a) and 4(b) show that the amplitude of the piezocharge distribution at the metal–MoS_2 interface is larger than that at the free-standing MoS_2 sheet. In the free-standing MoS_2 sheets, the free metallic electrons at the MoS_2 surfaces around the MoS_2 sheet can easily flow under the piezoelectric field, thus screening the piezopotential in the MoS_2 sheet. In contrast, the electrons at the

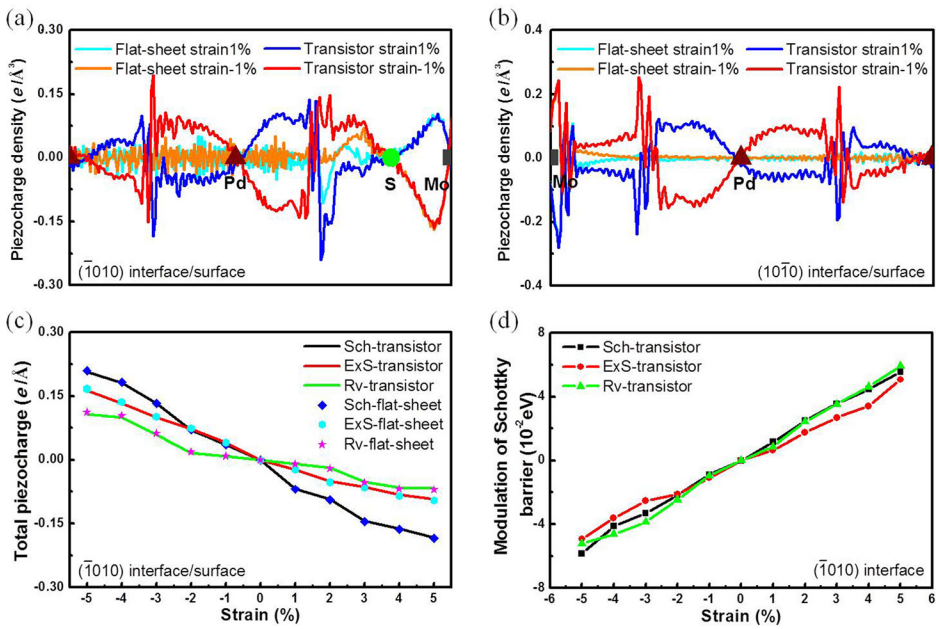

FIG. 4. (a) Piezocharge distribution of the Sch-transistor and the corresponding free-standing MoS_2 sheet at the $(\bar{1}010)$ interface/surface under applied strain of $\pm 1\%$; (b) piezocharge distribution of the Sch-transistor and the corresponding free-standing MoS_2 sheet at the $(10\bar{1}0)$ interface/surface under applied strain of $\pm 1\%$; (c) total piezocharge per transistor/sheet width of the Sch-, ExS-, and Rv-transistors and the corresponding free-standing MoS_2 sheets at the $(\bar{1}010)$ interface/surface; and (d) modulation of the Schottky barrier heights of the Sch-, ExS-, and Rv-transistors at the $(10\bar{1}0)$ interface. In (a) and (b), the brown triangles indicate the relative positions of the Pd atoms, the green circles indicate the relative positions of the S atoms and the grey squares indicate the relative positions of the Mo atoms along the z-axis.

interfaces in the transistors become bound electrons and lose the ability to redistribute under the piezoelectric field, which demonstrates the piezoelectric polarization.

In summary, using DFT calculations, we have determined the transition of the single-layer MoS_2 edge electronic states from metallic states to semiconductive states by contact with metal electrodes, which form metal–MoS_2 interface structures and exhibit both piezoelectric and piezotronic effects. By relating the piezotronic effect to the interface electronic structure, we have revealed the essential role of the metal–MoS_2 interface structure in preserving the piezotronic effect.

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[1]Z. L. Wang and J. Song, Science **312**, 242 (2006).
[2]Z. L. Wang, *Piezotronics and Piezo-Phototronics* (Springer, Berlin, Heidelberg, 2013).
[3]R. Yu, W. Wu, C. Pan, Z. Wang, Y. Ding, and Z. L. Wang, Adv. Mater. **27**, 940 (2015).
[4]W. Wu, X. Wen, and Z. L. Wang, Science **340**, 952 (2013).
[5]C. Pan, L. Dong, G. Zhu, S. Niu, R. Yu, Q. Yang, Y. Liu, and Z. L. Wang, Nat. Photonics **7**, 752 (2013).
[6]W. Wu, L. Wang, Y. Li, F. Zhang, L. Lin, S. Niu, D. Chenet, X. Zhang, Y. Hao, T. F. Heinz, J. Hone, and Z. L. Wang, Nature **514**, 470 (2014).
[7]K.-A. N. Duerloo, M. T. Ong, and E. J. Reed, J. Phys. Chem. Lett. **3**, 2871 (2012).
[8]M. V. Bollinger, J. V. Lauritsen, K. W. Jacobsen, J. K. Nørskov, S. Helveg, and F. Besenbacher, Phy. Rev. Lett. **87**, 196803 (2001).
[9]M. V. Bollinger, K. W. Jacobsen, and J. K. Nørskov, Phy. Rev. B **67**, 085410 (2003).
[10]C. Gong, L. Colombo, R. M. Wallace, and K. Cho, Nano Lett. **14**, 1714 (2014).
[11]Y. Dong and L. J. Brillson, J. Electron. Mater. **37**, 743 (2008).
[12]S. Bertolazzi, J. Brivio, and A. Kis, ACS Nano **5**, 9703 (2011).
[13]G. Kresse and J. Hafner, Phy. Rev. B **48**, 13115 (1993).
[14]G. Kresse and J. Furthmüller, Phy. Rev. B **54**, 11169 (1996).
[15]P. E. Blöchl, Phy. Rev. B **50**, 17953 (1994).
[16]G. Kresse and D. Joubert, Phy. Rev. B **59**, 1758 (1999).
[17]J. P. Perdew, K. Burke, and M. Ernzerhof, Phy. Rev. Lett. **77**, 3865 (1996).
[18]I. N. Levine, *Quantum Chemistry* (Prentice Hall, New Jersey, 2000).
[19]H. Zhu, Y. Wang, J. Xiao, M. Liu, S. Xiong, Z. J. Wong, Z. Ye, Y. Ye, X. Yin, and X. Zhang, Nat. Nanotechnol. **10**, 151 (2015).
[20]W. Liu, A. Zhang, Y. Zhang, and Z. L. Wang, Nano Energy **14**, 355 (2015).