Supplementary Information

Piezoelectricity in WSe_2/MoS_2 Heterostructure Atomic Layers

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1. Energy band diagram of layered TMDCs

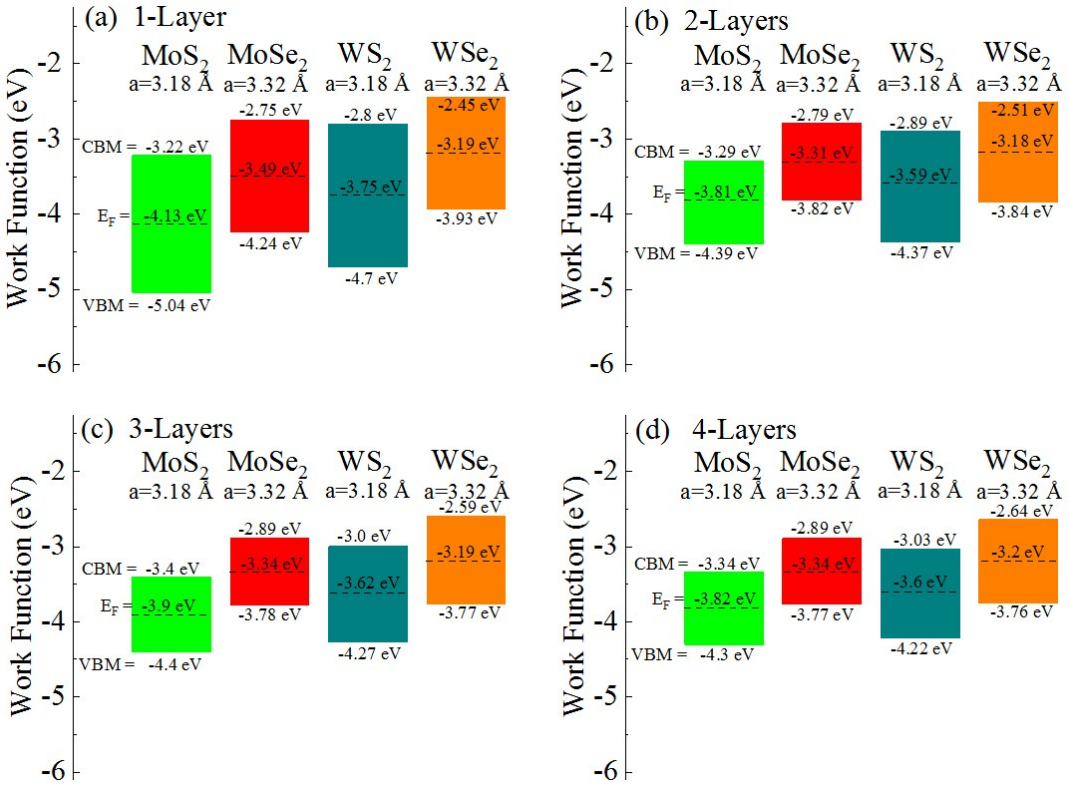

Figure 1s. Electronic band diagrams of TMDCs for (a) 1 layer; (b) 2 layers; (c) 3 layers, and (d) 4 layers. E_F indicates the Fermi energy level.

The electronic band diagrams of TMDCs with different number layers are shown in figure 1s. The forbidden band of each material is colored, where conduction band minimum (CBM), valence band maximum (VBM), and Fermi energy level (E_F) are numerated. The bandgap is reduced with the increasing number of atomic layers. The direct bandgap of monolayer changes to the indirect gap of multilayers. The direct band gap of TMDC monolayer is located at K and K' points in the first Brillouin Zone, and the electronic transitions are associated with valley pseudospin, electron and hole spins, and optical helicity. For the bilayer MoS_2, the VBM shifted from K to Γ[1]. The layer number-dependent band-structure is due to the quantum confinement along the c-axis of the atomic layers. The band-gap change $\Delta E_g = \frac{h^2\pi^2}{2ma^2}$ for film thickness was predicted by Sandomirskii in 1963, where a is the film thickness[2]. The chalcogenide (S, Se, and Te) ion with higher atomic

number has the bigger orbital radius and better coupling with the d orbitals of transition metal ions. Therefore, the CBM and VBM values of TMDC atomic layers are higher for the higher atomic number of chalcogenide ions with a specific transition metal ion. The CBM and VBM values of TMDC monolayer are also determined by the d-orbital of cation. Since the $5d^2$ orbital energy of W cation is higher than the $4d^2$ orbital energy of Mo cation, the CBM and VBM values of WX_2 are higher than those values of MoX_2 for the specific chalcogenide ion[3]. The WSe_2/MoS_2 heterostructure is favorable for piezoelectronics because of the larger band offset between the CBM of n-type MoS_2 atomic layer and the VBM of p-type WSe_2 atomic layer, and the larger electronic polarization between p-type and n-type atomic layers than the band offset and electronic polarization of the other heterostructures with W and Mo cations and S and Se anions.

2. Layer angle-dependent piezoelectricity of heterostructure

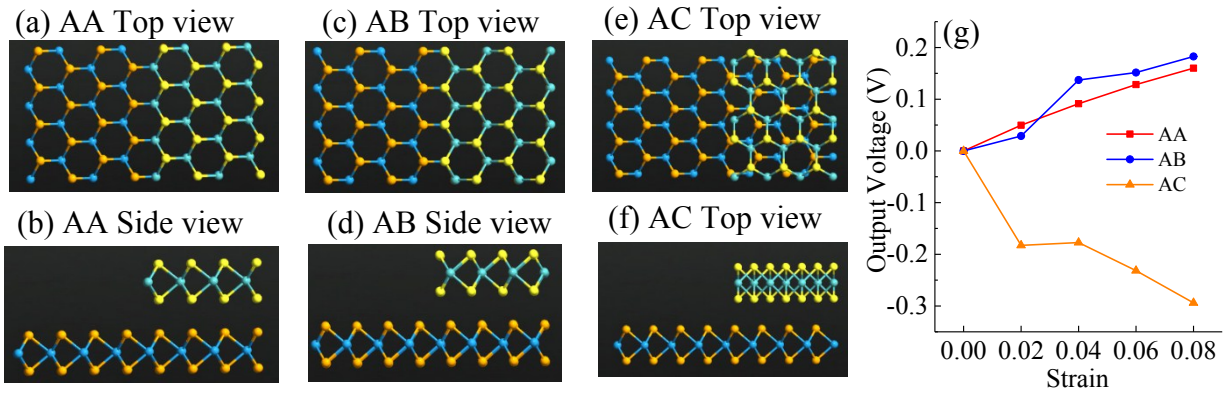

Figure 2s. (a), (b), (c), (d), (e), and (f) Schematic drawings (top view and side view) of WSe_2/MoS_2 heterostructures for AA-, AB- and AC-stacking for different lattice positions between p- and n-type layers. (g) Output voltage as a function of tensile strain for AA-, AB- and AC-types of layer arrangement.

The lattice position and the orientation angle between layers in heterostructure are the deterministic conditions of piezoelectricity. As it was aforementioned, the piezoelectricity of AB-stacking heterostructure is larger than that of AA-stacking heterostructure due to the higher internal ionic polarization of AB-stacking than that of AA-stacking. In both AA- and AB-stacking heterostructures, the armchair direction is aligned along the transport direction as shown in figure 2s (a), (b), (c), and (d). However, in the AC-stacking heterostructure where MoS_2 layer is rotated 90 degrees with respect to the WSe_2 monolayer as shown in figure 2s (e) and (f), where the zigzag direction of MoS_2 monolayer is aligned along the transport direction, while the armchair direction

of WSe_2 monolayer is aligned along the transport direction. Figure 2s (g) shows the output voltage as a function of strain for three different styles of AA-, AB-, and AC-stacking. AC-stacking heterostructure has the highest output voltage of 0.284 V in absolute value for the 8% tensile strain. The output voltage is delineated as the electrostatic potential difference between the strained and the unstrained heterostructures. The positive output voltage of AA- and AB-stacking heterostructure indicates that the electric potential of strained heterostructure is larger than that of unstrained one. The output voltage polarity of AC-stacking heterostructure was reversed with respect to that of AA- and AB-stacking heterostructure. It implies that the electric potential of strained AC-stacking heterostructure is much smaller than that of unstrained one.

References

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3. A. Pant, Z. Mutlu, D. Wickramaratne, H. Cai, R. K. Lake, C. Ozkan and S. Tongay, *Nanoscale*, 2016, **8**, 3870–3887.