Tuning the Conductivity Type in Monolayer WS$_2$ and MoS$_2$ by Sulfur Vacancies

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While $n$-type behavior appears to be more common in as-prepared two-dimensional (2D) transition metal dichalcogenides (TMDCs), substitutional doping with electron accepting atoms is typically required to tune the conductivity to $p$-type in order to facilitate their potential application in different devices. Herein, a systematic study is reported on the equivalent electrical “doping” effect of single sulfur vacancies (V$_{1S}$) in monolayer WS$_2$ and MoS$_2$ by studying the interface interaction of WS$_2$–Au and MoS$_2$–Au contacts. Based on the first principles calculations, it is found that the V$_{1S}$ can significantly alter the semiconductor behavior of both monolayer WS$_2$ and MoS$_2$ so that they can exhibit the character of electron acceptor ($p$-type) as well as electron donor ($n$-type) when they are contacted with gold. For relatively low V$_{1S}$ densities (approximately <7% for MoS$_2$ and <3% for WS$_2$), the monolayer TMDC serves as electron acceptor. As the V$_{1S}$ density increases beyond the threshold densities, the MoS$_2$ and WS$_2$ play the role of electron donor. The significant impact V$_{1S}$ can have on monolayer WS$_2$ and MoS$_2$ may be useful for engineering its electrical behavior and offers an alternative way to tune the semiconductor TMDCs to exhibit either $n$-type or $p$-type behavior.

As a member of transition metal dichalcogenides (TMDCs), 2D tungsten disulfide (WS$_2$) has attracted enormous interests due to its attractive properties for potential applications in electrical and optical fields, especially in the field of low-power field-effect transistors (FETs), photodetectors, gas and chemical sensors, memory and electroluminescent devices, and integrated circuits. pristine WS$_2$ is reported to be an $n$-type semiconductor. Ovchinnikov et al. fabricated FETs based on single layers semiconductor WS$_2$ and reported $n$-type behavior with a high on/off current ratio of $\approx 10^6$ at room temperature. In addition to $n$-type behavior, Morrish et al. reported that semiconducting WS$_2$ layers showed an indirect bandgap of 1.4 eV and an absorption coefficient of $\approx 5 \times 10^4$ cm$^{-1}$. While $n$-type behavior appears to be more common in as-prepared two-dimensional (2D) transition metal dichalcogenides (TMDCs), $p$-type behavior.

To realize the attractive properties in potential applications, significant efforts have been directed to tune the properties of WS$_2$. Doping, which can controllably tailor both the material’s crystalline structure as well as bandgap, is one of the most common procedures that has been widely demonstrated both theoretically and experimentally. Iqbal et al. showed an unprecedented high mobility of 235 cm$^2$/V·s at room temperature in a WS$_2$ FET fabrication by $n$-type chemical doping of WS$_2$ films. Shi et al. synthesized Co-doped WS$_2$, and they used both calculations and experiments to demonstrate that the Co-doped WS$_2$ was more active for the hydrogen evolution reaction compared with pristine WS$_2$.

Azizi et al. synthesized striped triangular monolayer flakes of W$_x$Mo$_{1-x}$S$_2$ and found in them both spin–orbit and thermal transport anisotropies.

For semiconducting TMDCs, some recent works have reported methods for $n$-type doping, such as hydrogen adsorption on TMDCs and chemisorption of oxygen on surface defect MoS$_2$. It is also important to effectively dope the TMDCs as $p$-type for their potential application in 2D-semiconductor-based complementary metal–oxide–semiconductor (CMOS)-FETs. Currently, most TMDC logic circuits are based only on $n$-channel metal–oxide–semiconductor FETs (MOSFETs). The $p$-type TMDC is also important in photodiodes and light-emitting devices as well as other $p$–$n$ junction-based optoelectronic devices. Jin et al. demonstrated that substitutional doping of WS$_2$ with Nb changes the carrier type, switching the WS$_2$ transport behavior from intrinsic $n$-type to $p$-type. In addition, it was found that the bandgap and their optical properties can be tuned by carefully controlling the Nb density. Laskar et al. showed that Nb can also be used as $p$-type dopant in MoS$_2$. Tang et al. reported that the electrical characteristics of monolayer/few-layer WS$_2$ FETs clearly show an $n$-channel to $p$-channel conversion with nitrogen incorporation. Similarly, Avcial et al. demonstrated that $p$-type doping of MoS$_2$ is attained by substitutional nitrogen doping. Furthermore, various reports have shown that $p$-type doping behavior can also be
obtained by introducing carbon to monolayers of WS$_2$,[21] phosphorus to MoS$_2$,[22] and oxygen adsorption to MoS$_2$.[23] However, these doping methods pose major concerns in terms of crystal stability, impurity, and structural damage (or even etching) by energetic ions, particularly for monolayers.[24,25] Hence, recent works have also investigated alternative methods for tuning the electrical transport properties of TMDC monolayers without the introduction of foreign atomic species. One example is to use the charge transfer arising from different types/densities of sulfur vacancies on monolayer MoS$_2$ to create a $p$-type or $n$-type semiconductor/metal contact.[26]

We present, herein, a method to endow monolayer WS$_2$ or MoS$_2$ with both electron acceptor ($p$-type) and electron donor ($n$-type) behaviors in conjunction with the use of Au as contact to the monolayer TMDC. A single sulfur vacancy ($V_{1S}$) is introduced into unit cells of different sizes to mimic different $V_{1S}$ defect densities. We find that even though the intrinsic WS$_2$ behaves like an $n$-type semiconductor once in contact with metal, the introduction of 1.6% $V_{1S}$ (density of $1.8 \times 10^{13}$ cm$^{-2}$) can induce a charge transfer behavior similar to a $p$-type doping. As the density of $V_{1S}$ is increased to $7.1 \times 10^{13}$ cm$^{-2}$ or 6.3% and beyond, it switches again to an $n$-type behavior. The charge transfers associated with such $V_{1S}$ appear correlated with the energy offset between the conduction band minimum (CBM) and the unoccupied defect state. We find this association to be consistent and generalizable to the case of MoS$_2$ as well. Our results indicate defect engineering as an effective method for controlling the electronic properties of TMDC monolayer interfaced with metals without the need of foreign atom introduction. Such TMDC–metal interfaces are commonly found at the source/drain contact regions of devices and are crucial design considerations for efficient carrier injection.

All the studies were performed using the plane-wave technique implemented in Vienna ab initio simulation package.[27,28] The generalized gradient approximation with the Perdew–Burke–Ernzerhof (PBE) functional has been used to describe the exchange–correlation potential in all calculations.[29,30] While hybrid functionals [e.g., Heyd–Scuseria–Ernzerhof (HSE) and PBE0] may be used for obtaining more accurate band structures, they are computationally more demanding than the traditional PBE functional. Considering that the hybrid functionals, such as HSE and PBE0, do not change the general trend,[31,32] the PBE functional was applied in this study as a compromise between the computational cost and the accuracy. To study how the interface interaction at Au(111)–WS$_2$ and Au(111)–MoS$_2$ contacts is influenced by $V_{1S}$ (as shown in Figure 1), 2 × 2, 4 × 4, 6 × 6, and 8 × 8 supercells were constructed, which mimics the $V_{1S}$ density of 25%, 6.3%, 2.8%, and 1.6%, respectively. As the convergence test for k-points showed that the charge transfer result is not sensitive to different k-points, a 2 × 2 × 1k-point mesh was used for all Au–WS$_2$ and Au–MoS$_2$ systems. For isolated WS$_2$ and MoS$_2$, we applied a 9 × 9 × 1k-point mesh for more accurate band structure analysis. The cutoff energy was set to be 500 eV. A 25 Å vacuum layer was used to separate the periodic slab in vertical direction for all interface structures. The van der Waals interactions is corrected with

Figure 1. The optimized structures of Au–WS$_2$ and Au–MoS$_2$ contacts with various $V_{1S}$ densities: a) 0%, b) 1.6%, c) 2.8%, d) 6.3%, and e) 25.0%. The top panel represents the supercell structures; the middle panel represents the Au–WS$_2$ interfaces, and bottom panel represents the Au–MoS$_2$ interfaces. Yellow, gray, purple, and green spheres represent S, Au, Mo, and W atoms, respectively. As shown in (a), the distance between the topmost S layer and the bottom Au layer is defined as the interface thickness.
Grimme’s dispersion-corrected density functional theory (DFT-D2) method. All structures were optimized until the Hellmann–Feynman force on each atom was smaller than 0.05 eV Å⁻¹.

We used electron density difference map and Bader charge transfer amount to evaluate the contact–TMDC interaction at the interface. The electron density difference map is defined as the electron density difference before and after the contact between Au and TMDCs

\[
\Delta \rho = \rho_{\text{Au–MoS}_2} - \rho_{\text{Au}} - \rho_{\text{MoS}_2}
\]

so that it can directly visualize the direction and amount of electron movement. The Bader charge calculations were carried out to evaluate the amount of charge transferred between Au and TMDC. If electrons are transferred from the metal to the TMDC upon contact, the TMDC acts as an electron acceptor, which corresponds to p-type behavior. On the other hand, if electrons are transferred from the TMDC to the metal, the TMDC acts as an electron donor, which corresponds to n-type behavior.

To gain more insight into the effect of V₁₅, we also determined the energy offset \( \Delta E \) defined as the energy difference between the CBM and the maximum of the unoccupied defect state

\[
\Delta E = E_{\text{CBM}} - E_{\text{unoccupied defect state maximum}}
\]

The Au–WS₂ and Au–MoS₂ interfaces were first evaluated by physical separation and then by the electron density difference and Bader charge calculations. These are followed by a detailed study on the band structure of monolayer WS₂ and MoS₂, focusing on the effect of various V₁₅ densities.

The optimized structures of the Au–WS₂ and Au–MoS₂ interface systems with various V₁₅ densities are shown in Figure 1. The physical separation \( d \), as shown in Figure 1a, is defined as the thickness of the interface. A thinner interface with smaller \( d \) value suggests a potentially more orbital overlap at the interface and, hence, the formation of stronger bond, such as covalent bond. For Au and pristine WS₂, the calculated \( d \) is 2.37 Å, which is 0.11 Å larger than the sum of the S and Au covalent radii, resulting in a limited orbital overlap and very weak interaction between WS₂ and Au. This is in line with a previous study, which claims that the interaction between Au and WS₂ is considered as physical adsorption, and there is no obvious electron overlap between the bottom S atoms and the top Au atoms. Similar weak interaction is also detected in the Au–MoS₂ contact. Upon the creation of the V₁₅, there are rearrangements of the Au atoms, as shown in Figure 1b–e. The rearrangement of interface Au atoms becomes more significant, as the V₁₅ density increases from 1.6% to 25.0% for both Au–WS₂ and Au–MoS₂.

We carried out the electron density difference map and charge transfer amount calculations to evaluate the Au–WS₂ and Au–MoS₂ contact interfaces. The top panel of Figure 2a shows the electron density difference map associated with the interaction between pristine WS₂ and Au. Although there is electron movement upon interaction, it is not sufficient to conclude the overall electron transfer direction. To investigate on the charge transfer in detail, Bader charge calculation was performed. The results suggest that the electron transfer direction is from WS₂ to Au, and the charge transfer amount is \( \tfrac{1}{2} \times 10^{-2} e^- \) per surface Au atom. In other words, the monolayer WS₂ serves as an electron donor, leading to an n-type contact with Au. This is in line with the experimental FET results, which identified electrons as majority carriers in pristine monolayer WS₂.[6,7] The top panel of Figure 2b shows the electron density difference map associated with the contact between Au and WS₂–V₁₅. Upon the creation of V₁₅, charge disorder is created at the interface, and the electrons tend to accumulate around the missing S atoms site. This is observed in the top panel of Figure 2b where the charge accumulation and depletion

![Figure 2](https://www.advancedsciencenews.com/doi/abs/10.1002/pssr.202000248)
areas (blue and purple, respectively) are slightly distorted compared with the pristine case, and some charge accumulations are seen in WS₂ layer. The electron movements from Au to WS₂–V₁S indicate that the WS₂ with a density of 1.6% V₁S serves as an electron acceptor, and thus, the V₁S induces an overall p-type behavior in the monolayer WS₂. The amount of charge transfer evaluated by the Bader charge analysis is 2.8 × 10⁻² e⁻ per surface Au atom. This introduction of a relatively small number of defects can tune its conductivity type to electron acceptor with respect to the defect-free WS₂. A possible reason for its p-type behavior is that the deep defect states created by the sulfur vacancies may act as electron-trap centers. A similar effect is detected when V₁S density is further increased to 2.8%, as shown in the top panel of Figure 2c. However, the charge transfer amount is reduced to 0.79 × 10⁻² e⁻ per surface Au atom, indicating a reduced p-type behavior compared with 1.6% V₁S. When the V₁S density is increased to 6.3%, as shown in the top panel of Figure 2d, the electron movement becomes more substantial but in the opposite direction. Instead of accumulating around the defect site, the electron tends to migrate toward Au layers, indicating that the WS₂–V₁S acts as an electron donor, and the V₁S appears to have an effect similar to an n-type doping. The amount of charge transfer is calculated to be 1.19 × 10⁻² e⁻ per surface Au atom. One possible explanation is that as the unsaturated electron associated with the sulfur vacancy is located on neighboring W atoms, the number of unsaturated electrons on W atoms increases when the defect density is increased. This makes the WS₂ electron rich and serves as the source of electron carriers. This explanation is also applicable for Au–WS₂ with 25% V₁S. With more missing S atoms, there are more unsaturated electrons and make the WS₂ more electron-rich. As shown in Figure 2e, the relevant amount of charge transferred from WS₂ to Au increases significantly to 7.0 × 10⁻² e⁻ per surface Au atom. This is in line with previous work, which showed that the sulfur vacancy produces an n-type doping effect.

We have performed a similar analysis for the effect of V₁S on MoS₂. As shown in the bottom panel of Figure 2a, there is hardly any charge redistribution upon the contact of Au and pristine MoS₂, indicating a weak interaction between them. V₁S makes the MoS₂ electron-poor when its density is 1.6%, and this trend continues to a density of 2.8%. Although the charge transfer amount slightly increases for V₁S density of 6.8%, the electron transfer direction is still from Au to MoS₂. This is in line with the report that the native sulfur vacancies in MoS₂ generate deep levels below the CBM and make it act as an electron-trap center. When the V₁S density is increased to 25%, the MoS₂ becomes electron donor, suggesting that the V₁S is producing an effectively n-type doping behavior. This agrees with previous work claiming that the sulfur vacancy is a sufficiently shallow electron donor state resulting in n-type monolayer MoS₂.

In addition, theoretical evidence supports that sulfur vacancies that exist in MoS₂ introduce localized donor states inside the bandgap. The fact that MoS₂ can switch its role between electron acceptor and electron donor agrees with our previous study as well as the experimental study reporting that MoSₓ experienced a transition from p-type to n-type as the ratio of S:Mo decreases.

From the electron density difference map and Bader charge calculation, we, therefore, find that the charge transfer direction between WS₂ or MoS₂ and Au can be tuned by varying the V₁S density. In other words, the “doping” effect can be switched between p-type and n-type behaviors for both WS₂ and MoS₂ by tuning their sulfur vacancy density. The amount of charge transfer per surface Au atom as a function of the V₁S density is summarized in Figure 3. Once in contact with Au, the pristine WS₂ tends to acquire charge from the metal layers, thus behaving as an n-type semiconductor, whereas the pristine MoS₂ is an intrinsic semiconductor. Upon the creation of a relatively small amount of V₁S, both WS₂ and MoS₂ become electron acceptor, inducing a p-type semiconductor behavior. As the V₁S density is increased beyond their respective threshold densities, both exhibit n-type behavior. In general, for a highly defective system, V₁S leads to the WS₂ or MoS₂ having an electron donor (n-type) behavior, whereas for a system with sufficiently low defect densities, V₁S can induce a p-type behavior. For a given contact metal, the crossover V₁S density is dependent on the TMDC material.

To further understand why different V₁S densities can produce p- or n-type behavior, a detailed study on the band structure was performed, focusing on the defect states. The band structures of monolayer WS₂ and MoS₂ with various V₁S densities are summarized in Figure 4. The bandgap of pristine monolayer WS₂ is direct and about 1.80 eV, which agrees well with the literature. The existence of V₁S results in the generation of defect states at the bandgap regions (as shown in Figure 4b–e). With a V₁S density of 1.6%, an unoccupied defect state is introduced, with an energy offset of 0.40 eV between the CBM and the top of unoccupied defect state. The deep defect states created by the sulfur vacancies prohibit them from acting as electron donors, so that they do not contribute to more n-type behavior.

![Figure 3. The effect of V₁S density in MoS₂ and WS₂ on interface charge transfer. The charge transfer amount is represented as per surface Au atom to allow comparison between different defect densities. Green and pink dots correspond to Au–MoS₂ and Au–WS₂ interfaces, respectively. A positive charge transfer amount indicates the electron movement from TMDCs to the metal and suggests an n-type behavior of the TMDCs, and a negative charge transfer denotes the opposite direction, indicating a p-type behavior of the TMDCs.](image-url)
As the V1S densities increase, these two unoccupied defect states gradually split into two, and the energy offset changes to 0.42 eV (2.8%), 0.37 eV (6.3%), and 0.06 eV (25.0%) for each V1S density. For pristine monolayer MoS2, it has a direct bandgap of about 1.84 eV, which is in line with previous DFT calculations. At the same V1S density, the absolute energy offset of the defect state is larger for MoS2 than that of WS2 while the trend is the same. The energy offset is 0.58 eV for a V1S density of 1.6%. As the density of V1S is increased, the unoccupied defect states split, and the energy offset becomes 0.54 eV (2.8%) and 0.59 eV (6.3%) and then reduces to 0.21 eV (25.0%).

The amount of charge transfer (per surface Au atom) as a function of unoccupied defect state energy offset ($\Delta E = E_{CBM} - E_{unoccupied\ defect\ state\ maximum}$) is summarized in Figure 5. For WS2 with a V1S density of 1.6% and 2.8%, large energy offsets of 0.40 and 0.42 eV are observed, respectively. These deep unoccupied defect states below the CBM might prohibit them from acting as an electron donor but make them more conducive and act as an electron acceptor ($p$-type behavior). For higher V1S densities (6.3% and 25.0%), smaller energy offset is observed, which favors an $n$-type behavior. A similar trend is found in MoS2: for $n$-type behavior (density of 25% V1S), the energy offset is small (0.21 eV); for $p$-type behavior (density of 1.6%, 2.8%, and 6.3% V1S), the energy offsets are relatively large (0.58, 0.59, and 0.54 eV). A similar reasoning may explain why the 6.3% density V1S case demonstrates an $n$-type behavior in WS2 but $p$-type in MoS2. In MoS2, the unoccupied defect state of 6.3% V1S is deep below the CBM, about 0.54 eV from the CBM. The unoccupied state is sufficiently low in energy, so that it favors electron injection. On the contrary, the unoccupied defect state of 6.3% V1S is shallower in WS2 (0.37 eV below the CBM), which might explain its $n$-type behavior.

While offering another alternative for controlling the doping level, the increase in defect density can also impact on the charge mobility, as sulfur vacancies may act as scattering centers for the carriers injected into the TMDC monolayers. Therefore, a balance between these two effects must be carefully considered in designing TMDC-based device.

We have performed a systematic study on the equivalent electrical “doping” effect of single sulfur vacancies in monolayer WS2 and MoS2 by studying the interfacial interactions of WS2–Au and
MoS$_2$–Au contacts. Different defect densities were explored. Both monolayer MoS$_2$ and WS$_2$ demonstrate the possibility to switch between electron acceptor (p-type) and electron donor (n-type) behaviors when the V$_{1S}$ density is varied. For relatively low V$_{1S}$ densities (approximately $<$7% or $7.2 \times 10^{13}$ cm$^{-2}$ for MoS$_2$ and $<$3% or $3.1 \times 10^{13}$ cm$^{-2}$ for WS$_2$), the monolayer TMDC serves as an electron acceptor, suggesting that the V$_{1S}$ imparts p-type behavior to the TMDC. We use the energy offset ($\Delta E$) from the TDMCs CBM to the unoccupied V$_{1S}$ defect state to obtain more insight into the effect of varying the density of V$_{1S}$. When the $\Delta E$ is smaller, the unoccupied V$_{1S}$ defect state is closer to the TDMCs CBM, and the TMDC tends to act as an electron donor (n-type behavior). On the other hand, when the $\Delta E$ is larger, the unoccupied V$_{1S}$ defect state is further away from the TDMCs CBM, which would facilitate electron injection into the TMDC and result in the TMDC acting as the electron acceptor (p-type behavior). While we anticipate that real systems will be more complex, the possibility to induce both p- and n-type electrical behavior via V$_{1S}$ in monolayer MoS$_2$ and WS$_2$ offers a potential pathway to tune conductivity without the introduction of foreign atoms, and this work provides the first-order guidance as to how one might engineer these behaviors in TMDC materials.

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Conflict of Interest

The authors declare no conflict of interest.

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2D materials, band engineering, doping, semiconductors, vacancy defects

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