

Tuning the transport polarity of tungsten diselenide-based n-type FET to p-type by MoO₃ contact doping

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Abstract. Atomically thin tungsten diselenide (WSe₂) has emerged as a promising material for next-generation electronic and optoelectronic devices. The surface functionalization of molybdenum trioxide (MoO₃) improves the performance of WSe₂ FET. The strong hole doping from MoO₃ to WSe₂ was revealed by measuring the electrical properties of the FET and calculating the electron mobility of WSe₂ devices. We demonstrated effective P doping of MoO₃ on WSe₂ FET devices, and the hole mobility of WSe₂ FET devices was improved by 3 orders of magnitude after contact doping with MoO₃ at 3.2nm.

Keywords: Tungsten diselenide, MoO₃ contact doping, Transport polarity.

1. Introduction

With the development of integrated circuits (IC), the channel length in electronic components has gradually reached below 5nm, which makes the short channel effect of the device more and more serious. Theoretical research shows that the key to reduce the short-channel effect is to select ultra-thin and large bandgap semiconductors.

Two-dimensional (2D) atom-layered tungsten diselenide (WSe₂) is considered a promising channel material due to its ultra-thin thickness, complementary intrinsic band gap with silicon, high I_{on}/I_{off} ratio, and highly adjustable electronic and optical properties. However, according to a large number of studies on WSe₂ in recent years, the inherent electric properties of WSe₂ are not competitive enough compared with traditional semiconductors, so chemical or electrostatic doping is often used to optimize the device performance. However, these doping methods apply to the whole channel and may change the material properties. Therefore, contact doping is promising to improve the electrical properties while maintaining the intrinsic feature of 2D semiconductors.

Surface charge transfer doping is a method of altering the charge distribution on the surface of a material by introducing external impurities or compounds on the surface of the material, thereby altering the electronic structure and charge transfer behavior of the material. On the surface of the material, the distribution of electrons and holes will be affected by surface states, surface defects and surface adsorbents, resulting in uneven surface charge distribution. The purpose of surface charge transfer doping is to regulate the distribution of electrons and holes on the surface by introducing specific impurities or compounds, so as to change the electronic structure and charge transfer behavior of the material, and then affect the electrical, optical, chemical properties of the material. Surface charge transfer doping can be achieved by different methods, including ion implantation, sputtering deposition, chemical vapor deposition and other techniques. These methods can introduce specific impurities or compounds to the surface of the material, forming a doping layer. The impurities or compounds in the doping layer interact with the material atoms and change the electron energy level structure and charge transfer path of the material.

In short, surface charge transfer doping is a method to regulate the electronic structure and charge transfer behavior of the surface of the material by introducing external impurities or compounds, which can change the electrical, optical, chemical and other properties of the material.

2. FET OF tungsten diselenide

At the beginning, we planned to use monolayer WSe₂ to prepare field-effect transistors. However, due to the thin WSe₂ of monolayer (atomic force microscopy shows that the thickness of monolayer WSe₂ is 0.7 nm), it is easy to break down the WSe₂ when measuring the electrical properties of FET. Therefore, after several experiments and analysis, we finally decided to use a double-layer WSe₂ to make a field-effect transistor (atomic force microscopy characterises a thickness of 1.3 nm for a double-layer WSe₂).

In order to create a small layer of WSe₂ FET, selloff tape was used to mechanically peel WSe₂ sheets from massive WSe₂ crystals (HQ-graphene) and subsequently transferred to degraded P-type doped silicon coated with 300 nm SiO₂. The target WSe₂ was identified using a high resolution optical microscope (Nikon Eclipse LV100D). The polymethyl methacrylate (PMMA) photoresist is immediately spun onto the sample to prevent the flakes from degrading in air.

And according to relevant reports, double layer tungsten diselenide also has some advantages in nature compared to single layer tungsten diselenide. The double layer of tungsten diselenide is composed of two layers of tungsten diselenide, which interact with each other through van der Waals force to make the whole structure more stable. Double-layer tungsten diselenide has a large band gap, which makes it have better application potential in photoelectric devices, such as as photoelectric conversion devices or photodetector parts. Due to the interaction between the two layers of tungsten diselenide in the double-layer structure, electrons can be efficiently transmitted and coupled between the two layers, which helps to improve the performance of electronic devices.

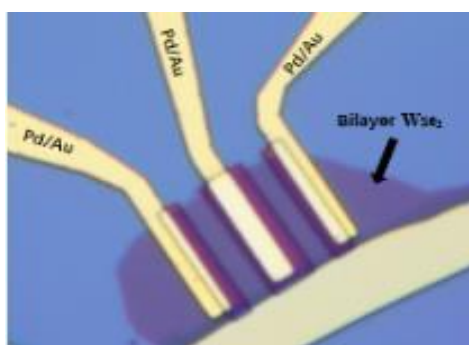


Figure 1. Optical image of a bilayer WSe₂ FET device.

Figure. 1 shows the optical microscope image of a WSe₂ FET prepared on a high P-doped silicon wafer with 300 nm SiO₂ as the dielectric layer and 10 nm Pd and 60 nm Au as the contact metals.

Different from single-layer two-dimensional materials, the multi-layer two-dimensional materials exhibit not only intra-layer vibration but also inter-layer vibration due to the existence of van der Waals interlayer interaction. The interlayer lattice vibration reflects the interlayer interaction of two-dimensional materials, and the interlayer interaction accumulated by different thicknesses is different, thus showing the thickness dependence of the interlayer vibration mode in the Raman spectrum, resulting in corresponding changes in the peak position, peak strength and peak shape of the Raman spectrum. Therefore, in this experiment, we can verify the layer number of WSe₂ through Raman spectroscopy.

In a single layer of tungsten diselenide, because there is only one layer of atoms, the electrons can only move in one plane, so its electronic structure shows two-dimensional characteristics. In the double layer of tungsten diselenide, because there are two layers of atoms, the electrons can move in two planes, so its electronic structure shows three-dimensional characteristics. These characteristics lead to the different optical properties of single and double layers of tungsten diselenide, and thus exhibit different photoluminescence spectra. The photoluminescence peak position of single-layer tungsten diselenide is about 700 nm, while that of double-layer tungsten diselenide is about 800 nm. Moreover, according to relevant reports, monolayer WSe₂ has only one peak in the photoluminescence spectrum between 1.4 and 1.7 eV, while multilayer WSe₂ has two peaks, as shown in Figure 2.

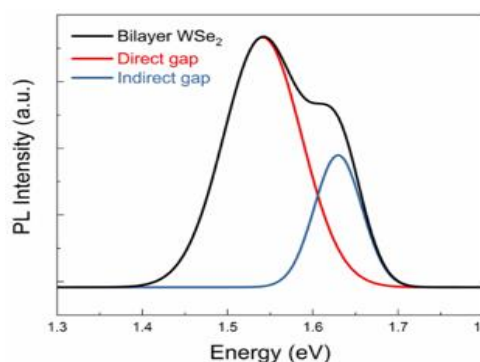


Figure 2. The Photoluminescence Spectroscopy of bilayer WSe₂.

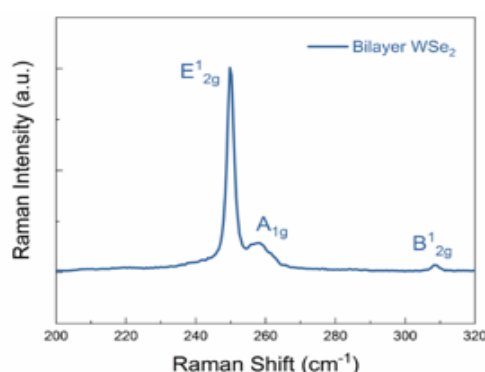


Figure 3. Raman spectrum of WSe₂.

Also in the Raman spectrum, the E_{2g} mode peak position of single-layer tungsten diselenide is about 251 cm⁻¹, while the E_{2g} mode peak position of double-layer tungsten diselenide is about 255 cm⁻¹. This is due to the interaction between the two layers in the double layer tungsten diselenide resulting in a slight shift in the E_{2g} mode. And in Figure 3, as reported, a B¹_{2g} peak of WSe₂ with a raman shift of 310cm⁻¹ can be seen, while this single-layer WSe₂ cannot be observed.

In summary, a field-effect transistor was constructed using a bilayer WSe₂, and Raman spectroscopy was used to verify the bilayer WSe₂. spectroscopy verified the two-layer WSe₂.

3. Contact hole doping by MoO₃

First of all, we will briefly explain the reasons for choosing MoO₃ as a doping material, there are three main aspects. First, energy level regulation: MoO₃ has high conductivity and transparency, and its bottom energy level of conduction band matches that of WSe₂, which can form a good alignment of energy levels. This energy level alignment can reduce the barrier between WSe₂ and the electrode, improve the efficiency of electron injection and extraction, and thus enhance the electron transport performance of the device. Second, charge transfer: MoO₃ has a high electron affinity and can be adsorbed on the surface of WSe₂ to form a charge transfer layer. This charge transfer layer can effectively adsorb and trap impurities and defects on the WSe₂ surface, reduce carrier scattering and recombination, improve carrier mobility and lifetime, and thus improve device stability and performance. Third, band regulation: the band structure of MoO₃ can regulate the band structure of WSe₂. By introducing MoO₃ modification layer, the band structure of WSe₂ can be changed, and the positions and shapes of its conduction and valence bands can be adjusted, thereby regulating the band structure and band gap of the device, optimizing the transport characteristics of electrons and holes, and improving the performance of the device.

As for the specific method of doping, in this experiment, we chose ion implantation method to dope moo3. The basic principle is: With an energy of 100keV, the ion beam incident into the material, the ion beam and the atoms or molecules in the material will have a series of physical and chemical interactions, the incident ion gradually loses energy, and finally stays in the material, and causes changes in the composition, structure and performance of the material surface, so as to optimize the

surface properties of the material, or obtain some new excellent properties. Compared with other methods such as vapor deposition, ion implantation method has certain advantages. The implanted ions directly combine with the atoms or molecules on the surface of the material to form a modified layer. The modified layer has no clear interface with the base material, and the binding is firm, and there is no phenomenon of falling off.

A PMMA layer was spin coated on the sample and we further used E-beam lithography to open the doping window near the electrode. Then contact doping with MoO_3 is completed through this window. The thickness of MoO_3 started from 0.8 nm, and the doping thickness doubled every time. Meanwhile, the performance change of WSe_2 device was measured by electrical detection equipment.

Figure 4 shows the schematic diagram of Surface transfer hole doping on WSe_2 devices by MoO_3 .

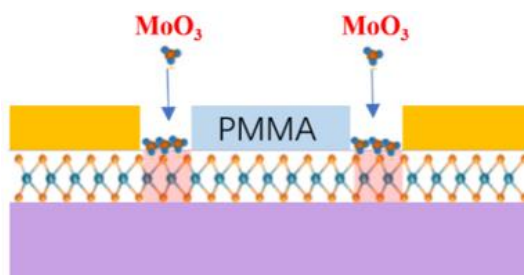


Figure 4. Surface transfer hole doping on devices.

As shown in Figure 5, where the gate voltage (V_g) sweeping from -80 V to 50 V and the source drain voltage (V_{sd}) fixed at 1V, doping of MoO_3 can significantly regulate the performance of WSe_2 FET. After deposition of MoO_3 , the current in electron side (positive V_g) gradually decrease while the current in hole side (negative V_g) gradually increase, reaching to 0.25 μA when the thickness of MoO_3 is 1.6 nm. With further deposition MoO_3 to 3.2 nm, the maximum current kept unchanged. This process indicates that MoO_3 doping can significantly consume electrons in WSe_2 FET device and tune its polarity from n-type to p-type.

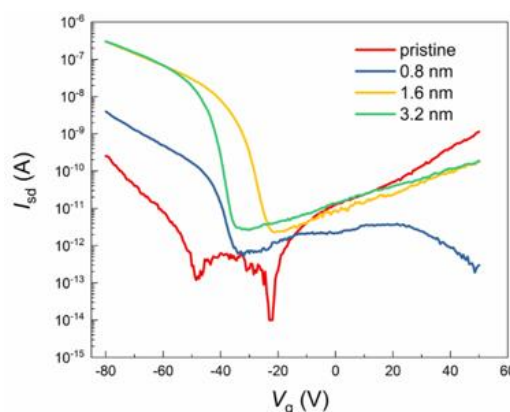


Figure 5. The change of WSe_2 FET transport characteristics with the increase of MoO_3 thickness from 0 to 3.2nm.

It is well known that the vacuum deposited MoO_3 thin film has a very high work function of 6.86eV and is essentially an N-type semiconductor, with EF located 0.2-0.3eV below the conduction band, which makes interface electrons transfer from WSe_2 to MoO_3 once physical contact is established between WSe_2 and MoO_3 . Therefore, the electron carriers in WSe_2 can be greatly depleted, which is consistent with our FET measurements in Figure 5.

As shown in Figure 6, when the gate voltage of the transistor is fixed at -80v and the V_{sd} is swept from -1 to 1v, it can be seen that the performance of the FET continues to improve with the increasing thickness of MoO_3 , and when the thickness of MoO_3 reaches 1.6nm, the output performance reaches the highest and the change trend gradually slows down. In addition, the steepness of the output characteristic curve reflects the response speed and sensitivity of the system or object. Therefore, under MoO_3 modification, WSe_2 FET is more sensitive to input signal changes and responds faster.

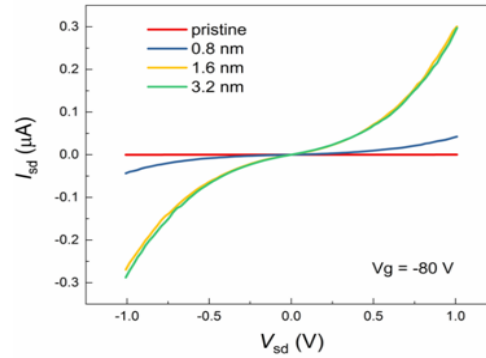


Figure 6. When V_g is fixed at -80V , output characteristic curve of WSe_2 FET under different deposition thickness of MoO_3 .

The work function of WSe_2 increases from 4.12 eV to 5.12 eV after deposition of MoO_3 at 0.1 nm (nominal thickness). As the thickness approaches 3.2 nm , the work function further increases due to the large amount of charge transfer between MoO_3 and WSe_2 and the formation of interfacial dipoles. This indicates that in MoO_3 -modified WSe_2 , EF moves toward the valence band of WSe_2 due to increasing hole concentration, resulting in significant upward band bending. After deposition at 0.8 nm , the band bending of MoO_3 reaches saturation, but the work function still increases due to the formation of interfacial dipoles caused by charge transfer.

Perhaps we can draw conclusions from a more intuitive perspective. Carrier concentration refers to the number of freely moving electrons or holes in a semiconductor material. It is one of the important parameters to describe the conductivity of semiconductor materials. The carrier concentration directly affects the conductivity of semiconductor materials. When the carrier concentration is higher, the conductivity of the semiconductor material will also increase accordingly, because the number of carriers is sufficient to conduct current more easily. In contrast, when the carrier concentration is low, the conductivity of the semiconductor material is reduced because the number of carriers is not sufficient to support efficient current transmission. In addition, the carrier concentration is also related to the doping concentration of the semiconductor material. Doping is the process of changing the electrical conductivity of a semiconductor material by introducing impurities into it. Doping can increase the carrier concentration in a semiconductor material, thereby improving its electrical conductivity. Common doping materials include phosphorus, boron, and arsenic and so on.

Therefore, we can calculate the carrier concentration of WSe_2 devices at different thicknesses of MoO_3 to determine the changes in their performance.

The hole mobility μ_h of the FET can be calculated from the formula (1), where L is the channel length and W is the channel width. C_i is the capacitance per unit area between WSe_2 and the back door, $C_i = \epsilon_0 \epsilon_r / d$, where ϵ_r and d are the dielectric constant and thickness of SiO_2 respectively, dI_{sd}/dV_g represents the maximum slope extracted from the linear region of the transfer feature.

$$\mu = \frac{L}{WC_i V_{sd}} \frac{dI_{sd}}{dV_g} \quad (1)$$

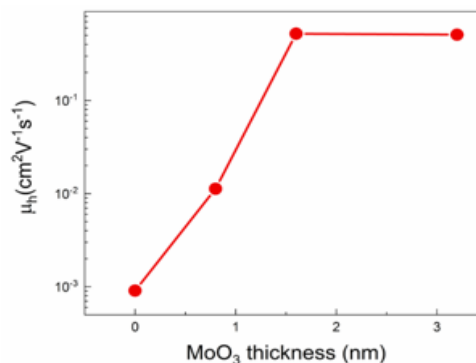


Figure 7. WSe_2 electron mobility with thickness of MoO_3 .

As shown in Figure 7, hole mobility calculation shows that after modification by 3.2nm MoO₃, the hole mobility of WSe₂ device increases by nearly 3 orders of magnitude, indicating that hole migration in WSe₂ channel is significantly improved.

However, it was noted that the hole mobility of WSe₂ device increased at a high rate before the thickness of MoO₃ reached about 1.6nm, and then there was almost no change, indicating that the modification effect of MoO₃ on WSe₂ devices in this experiment reached its limit at about 1.6nm.

4. Conclusion

Two-dimensional transition metal chalcogenides (TMDCs) are a kind of materials with special electronic structure and excellent electrical properties, and have become a research focus. In TMDCs devices, contact control is an important means to adjust device performance by selecting suitable metal materials and optimizing device structure. Therefore, the research on contact regulation of TMDCs has important theoretical and application value. So we hope that this study can play a certain role in the direction of contact regulation of two-dimensional transition metal chalcogenides.

Overall, we demonstrated effective P doping of MoO₃ on WSe₂ FET devices, and the hole mobility of WSe₂ FET devices was improved by 3 orders of magnitude after contact doping with MoO₃ at 3.2nm.

There are still many areas worth improving in this experiment, for example, the performance of the device can be improved. In the future plan, we plan to add a layer of BN between WSe₂ and the silicon chip, which is believed to improve the contact between materials, reduce the contact resistance, further improve the performance of the WSe₂ original device, and also increase the upper limit of the modification of MoO₃.

In summary, these results provide an easy way to effectively modify the transfer properties of WSe₂ based FET for its functional device applications.

References

- [1] Zhao W, Ghorannevis Z, Amara K K, Pang J R, T oh M, Zhang X, Kloc C, T an P H and Eda G 2013 Lattice dynamics in mono-and few-layer sheets of WS₂ and WSe₂ *Nanoscale* 5 9677.
- [2] Jo S H et al 2016 A high-performance WSe₂/h-BN photodetector using a triphenylphosphine (PPh₃)-based n-doping technique *Adv. Mater.* 28 4824
- [3] Lei B ,Zheng Y ,Hu Z , et al.Nondestructive hole doping enabled photocurrent enhancement of layered tungsten diselenide[J].*2D Materials*,2019,6(2):024002-024002.
- [4] Fang H, T osun M, Seol G, Chang T C, T akei K, Guo J and Javey A 2013 Degenerate n-doping of few-layer transition metal dichalcogenides by potassium *Nano Lett.* 13 1991
- [5] T osun M, Chan L, Amani M, Roy T, Ahn G H, T aheri P , Carraro C, Ager J W, Maboudian R and Javey A 2016 Air-stable n-doping of WSe₂ by anion vacancy formation with mild plasma treatment *ACS Nano* 10 6853
- [6] Zheng Y , Hu Z, Han C, Guo R, Xiang D, Lei B, Wang Y , He J, Lai M and Chen W 2018 Black phosphorus inverter devices enabled by in situ aluminum surface modification *Nano Res.* 12 531
- [7] Kröger M, Hamwi S, Meyer J, Riedl T, Kowalsky W and Kahn A 2009 P-type doping of organic wide band gap materials by transition metal oxides: a case-study on Molybdenum trioxide *Org. Electron.* 10 932
- [8] Lei B, Hu Z, Xiang D, Wang J, Eda G, Han C and Chen W 2017 Significantly enhanced optoelectronic performance of tungsten diselenide phototransistor via surface functionalization *Nano Res.* 10 1282