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Surface Doping and Humidity Sensing of MoS_2 Field-Effect Transistor by Oxygen Plasma Treatment

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Abstract: Two-dimensional (2D) semiconducting transition metal dichalcogenides (TMDs) have unique electrical, optical and mechanical properties, and hold great potential for diverse applications such as digital circuits, light harvesting and energy storage. Controlling the electrical properties of TMDs through doping provides an effective approach for sensitive sensing. This paper presents the experimental study of the doping effect of oxygen plasma on molybdenum disulfide (MoS_2). Firstly, the transport characteristics of the MoS_2 field-effect transistor (FET) were investigated and the MoS_2 FET exhibited p-type doping through plasma treatment. Then, the cause of the doping effect was further studied, and the doping effect was attributed to the formation of MoO_3-like defects on the surface of the channel, confirmed by Raman spectroscopy. Finally, the humidity-sensing behavior of the plasma-treated MoS_2 FET was studied. The MoS_2 FET exhibited high sensitivity to humidity because of the increased adsorption centers for water molecules, with the source-drain current change of approximately 54% in humid environment. The work would provide a simple method to modify the electrical properties of TMDs and show potential for low-dimensional chemical sensors.

Key words: field-effect transistor (FET); molybdenum disulfide (MoS_2); oxygen plasma; surface doping; humidity sensing
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0 Introduction

Two-dimensional (2D) materials have gained significant interest in the recent decades because of their excellent electronic, optical and mechanical properties related with unique layered architectures and band structures[1-4]. They have shown great potential in a host of device applications spanning from logic circuits, photodetectors and nonvolatile memories to sensors[5-8]. Among the 2D materials, molybdenum disulfide (MoS_2), belonging to the family of transition metal dichalcogenides (TMDs), is one of the most extensively studied 2D materials and considered to be a promising channel candidate of a field-effect transistor (FET) for next-generation electronics and optoelectronics[9-11]. Though MoS_2 exhibits a lower carrier mobility than zero-bandgap graphene, it enables a high on-off current ratio because of the non-zero bandgap for the MoS_2 FET. Moreover, due to the heavier effective carrier mass, MoS_2 shows better gate-tunable conductance and lower leakage current than silicon. Tremendous efforts have been made to study the fundamental physics of the MoS_2 FET. Meantime, to fulfill its practical and technological applications, it is critical to realize a full control over the charge carrier polarity and doping on MoS_2. By effectively tuning the basic properties of MoS_2, it could not only optimize the device performance, but also boost the functionalities of devices.

In traditional semiconductor FETs, ion implantation is a common tool to dope the semiconductors and tune the device characteristics[12]. However, this technique is not applicable to 2D materials because it would damage the crystals and degrade the device performance. In recent years, various chemical and physical doping techniques have been reported to tune the properties of 2D materials[13-15]. Among them, plasma treatment has been considered as a promising technique to enable the modification of materials in a time-efficient and cost-effective manner, and could tune the fundamental properties of 2D materials in terms of carrier mobility engineering, thickness control and surface functionalization[16-20]. Lee et al.[16] demonstrated the effectiveness of Ar plasma treatment for the oxygen desorption on the surface of the MoS_2 FET. The low-power Ar plasma treatment process effectively removes residual Cl, oxide layers and moisture during the MoS_2 thin film processing without significant etching and contamination risks. Kim et al.[17] utilized a low-intensity inductively coupled plasma source for oxygen plasma treatment of MoS_2. The treated MoS_2 FET exhibited high n-type doping and achieved layer thinning

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effects, and a promising method was provided for future applications. Yang et al.[18] investigated the electrical characteristics of a three-layer MoS_2 FET and a six-layer MoS_2 FET in a wide range of relative humidity (RH). They found that increasing the number of MoS_2 layers reduced the dependence of the conductive current on RH, while the hysteresis dependence on RH was not significantly altered, paving the way for future humidity-sensing applications.

In this work, the oxygen plasma treatment is demonstrated to have a p-type doping effect on the multilayer MoS_2 back-gated FET. The transport characteristics of the MoS_2 FET are measured and the shift of the carrier mobility as well as the threshold voltage is further exhibited. To reveal the cause of the p-type doping effect, Raman spectroscopy is conducted. The humidity sensitivity of the MoS_2 FET before and after plasma treatment is further measured and compared.

1 Experiments

1.1 Device fabrication

Multilayer MoS_2 nanosheets were micromechanically exfoliated by a tape on the top of the p-type doped Si substrate with a thick SiO_2 layer (a thickness of 300 nm). The source and drain electrodes were fabricated by UV lithography (MA6, SSUS, Germany) and e-beam evaporation (Ei-5z, ULVAC, Japan) and followed by the acetone lift-off procedure. The MoS_2 FET were annealed at 200 ℃ in vacuum for 2 h to improve the contact. For the plasma treatment, oxygen plasma (Diener Zepto, Diener electronic, Germany) with a constant power of 150 W for 3 min was employed. During the plasma exposure, the working pressure was 80 Pa.

1.2 Device characterization

Raman spectra of MoS_2 were obtained by confocal microscopic systems (Ntegra Spectra NT-MDT, Russia) with a 532 nm solid-state laser as the excitation source. The thickness of MoS_2 was measured by an atomic force microscope (AFM, MFP-3D Bio, Asylum Research, USA). The current-voltage measurements of the MoS_2 FET were performed by a semiconductor parameter analyzer (B1500A, Agilent, Germany) in a probe station at room temperature. For the humidity-sensing experiment, a humidifier and a hydrometer with remote probes were used to modify RH in the chamber. To avoid the influence of light illumination on the electrical performance of the MoS_2 FET, all the electrical experiments were carried out in dark environment.

2 Results and Discussion

2.1 Transport characteristics of MoS_2 FET

Figure 1(a) shows the schematic diagram of the MoS_2 FET with the exposure to oxygen plasma. As shown in Fig. 1(b), the multilayer MoS_2 with a thickness of 30 nm was selected as the channel in the MoS_2 FET. It is more suitable than the single-layer one for practical fabrication. Usually single-layer MoS_2 is easy to be damaged during the exposure of plasma treatment because of its ultrathin nature, which increases the fabrication difficulty. The inset in Fig. 1(b) is the optical microscope (OM, BX60M, OLYMPUS, Japan) image of a typical MoS_2 FET with a channel length of 8.5 nm and a channel width of 6.5 nm fabricated by a standard photolithography process. The metal electrode is comprised of a gold film (70 nm) with an adhesion layer of chromium (5 nm). According to the output curve of the MoS_2 FET, the relationship between the source-drain voltage V_{DS} and the current I_{DS} is linear and symmetric (Fig. 1(c)), demonstrating that the metal electrode forms ohmic contact with MoS_2. Then transfer curves of the MoS_2 FET were measured to investigate the doping effect of plasma treatment. Figure 1(d) shows the transfer curves of the MoS_2 FET by sweeping the back-gate voltages V_G from −20 V to 20 V at the source-drain voltage V_{DS} of 1 V. The current on/off ratio is about 10^5. Field-effect mobility μ is calculated by

$$\mu = [L/(WC_{ox}V_{DS})] \times (dI_{DS}/dV_G),$$

where L and W are the channel length and the channel width, respectively[21]; C_{ox} is the capacitance per unit area to the gate dielectrics and the value for 300 nm SiO_2 is 11.8 nF/cm^2.

For the untreated MoS_2 FET (black curve), it exhibits the n-type depletion mode and μ is 40.5 cm^2/(V·s), which is close to the previously reported results[10]. After exposing to oxygen plasma for 3 min, the MoS_2 FET was p-type doped (red curve). The oxygen atoms doped by plasma on top of MoS_2 exhibited a large electronegativity, acting as electron acceptors[22]. Consequently, the threshold voltage was raised to a higher value and on-current was reduced. However, after extending the exposure time to 10 min, the transfer curve remained stable. The cause may be the shallow penetration depth of oxygen atoms into MoS_2. Therefore, for the next experiments, the plasma treatment time was chosen to be 3 min.

The electron concentration n was calculated according to[23]

$$n = I_{DS}L/(eW\mu V_{DS}),$$

where e is elementary charge. It was calculated that the electron concentration changed from 4.63×10^{12} cm^{-2} to 2.51×10^{12} cm^{-2} after exposing to oxygen plasma. The threshold voltages extracted by extrapolating the linear portion of the transfer curves in a linear scale to a zero drain current is shown in Fig. 1(e). Figure 1(f) illustrates the specific value changes in the threshold voltage and the mobility of MoS_2 FETs before and after oxygen plasma treatment. It is observed that the threshold voltage shifts from −12 V towards −2 V, while the mobility of the MoS_2 FET is slightly reduced. In fact, the threshold voltage around the zero voltage is meaningful for practice logic circuits because of the reduced power consumption[24-25].

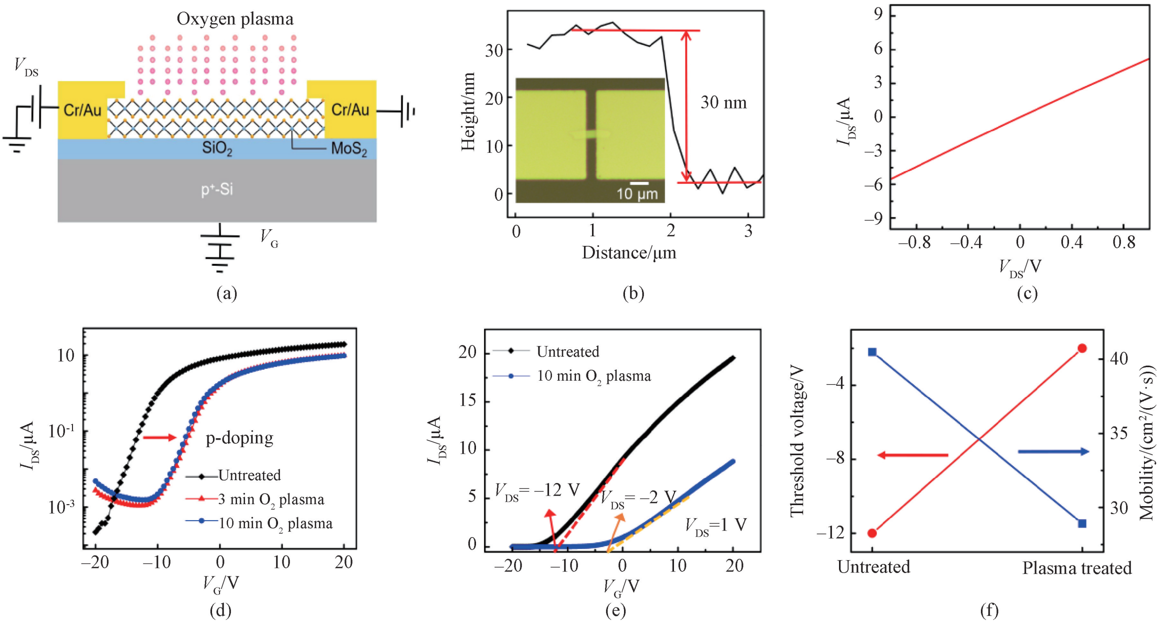


Fig. 1 Characterization and transport characteristics of oxygen plasma treated MoS_2 FET: (a) schematic diagram; (b) thickness of MoS_2 with optical microscope image of MoS_2 FET in inset; (c) output curve; (d) logarithmic scale and (e) linear transfer curves of untreated MoS_2 FET and oxygen plasma treated MoS_2 FET; (f) change of threshold voltage and mobility after oxygen plasma treatment

2.2 Doping mechanism

Raman spectroscopy was conducted to characterize the change of the channel after the plasma treatment. Figure 2(a) presents the in-situ Raman spectrum of the untreated MoS_2 FET. There are two prominent peaks around the wavenumber of 400 cm^{-1}, representing the in-plane vibration mode (E^1_{2g}) and the out-of-plane vibration mode (A_{1g}), respectively. The difference between the positions of the two peaks is about 25 cm^{-1}, corresponding to the feature of multilayer MoS_2[26-27]. In contrast, Fig. 2(b) displays the Raman spectrum of the MoS_2 FET treated with oxygen plasma. It can be observed that the position of the prominent peaks remains unchanged. Additionally, a small peak appears at the wavenumber of 225 cm^{-1}, and it is attributed to the formation of Mo—O bonds on the surface of the MoS_2 layer[28]. MoO_3-like defects act as electron acceptors, and the plasma treated MoS_2 FET obtains p-type doping effect.

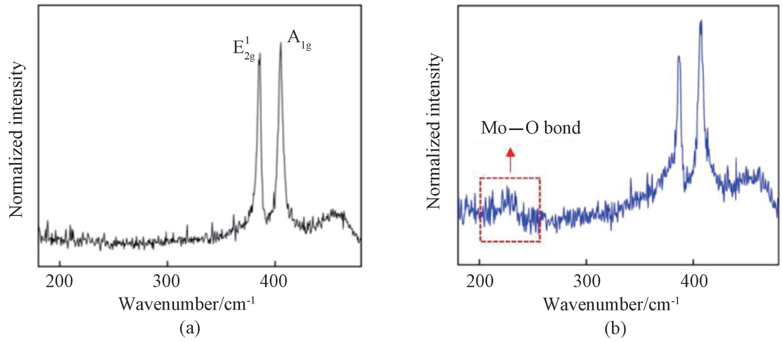
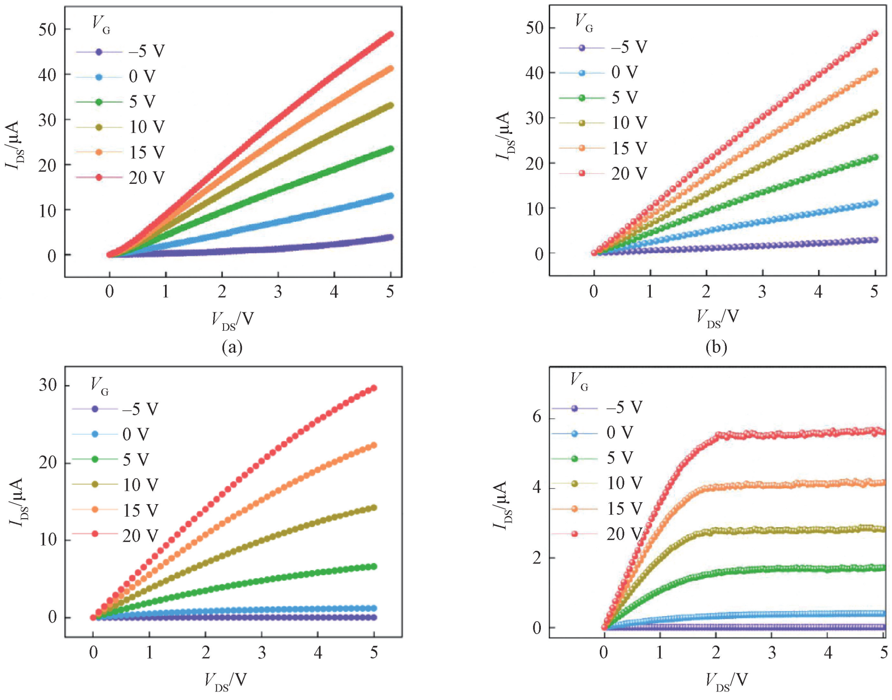


Fig. 2 Raman spectra of MoS_2 FET: (a) untreated; (b) oxygen plasma treated

2.3 Humidity-sensing performance

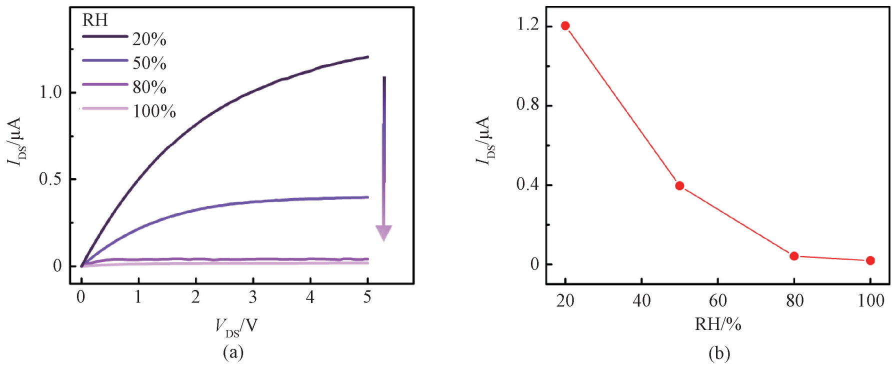
The output curves of the MoS_2 FETs before and after oxygen plasma treatment in humid environment (RH of 20% and 50%, respectively) are presented. As shown in Figs. 3(a) and 3(b), humidity almost has no influence on the output characteristics of the untreated MoS_2 FET, indicating good stability of the untreated MoS_2 FET even without passivation. After plasma treatment, the source-drain current slightly decreases and the turn-on voltage increases, which corresponds to the positive threshold voltage shift in the transfer curve. More interestingly, the treated MoS_2 FET is very sensitive to the humidity. According to Fig. 3(d), the I_{DS}-V_{DS} curve exhibits a linear triode regime at the low drain voltage and saturates at 2 V for all gate voltages, which is not observed in the untreated MoS_2 FET. According to the square law model of the transistor, the gate controls the saturation current under the pinched-off condition[29]. Therefore, the high-voltage gain can be achieved at this regime, which is essential for digital circuit. By comparing the current of the plasma treated MoS_2 in humid environment, the value decreases from 3.5 μA to 1.6 μA at $V_G = 5$ V and $V_{DS} = 2$ V with a change of approximately 54%, indicating a good humidity-sensing characteristic. The above results show that humidity only has a p-type doping effect on the oxygen plasma treated MoS_2 FET. Combining with the Raman spectrum measurement results, it is considered that the MoO_3-like defects act as adsorption centers for water molecules, and further enhance the p-type doping effect of MoS_2[30]. In comparison, the density of dangling bonds on the surface of the untreated MoS_2 is low, therefore, it is not susceptible to adsorbing water molecules and shows weak sensitivity. The sensing mechanism is different from the reported 2D material sensors based on Schottky junction in which humidity induces the change of the Schottky barrier height between the electrode and the semiconductor channel, resulting in the current change[31-32]. Because the fabricated FET exhibits ohmic contact, the effect of Schottky barrier change could be excluded.



(a) (b) (c) (d)

Fig. 3 Output curves: (a) untreated MoS_2 FET (RH of 20%); (b) untreated MoS_2 FET (RH of 50%); (c) oxygen plasma treated MoS_2 FET (RH of 20%); (d) oxygen plasma treated MoS_2 FET (RH of 50%)

Figure 4(a) illustrates the curves of I_{DS} as a function of V_{DS} at different RH values when $V_G = 0$ V. It can be observed that as RH increases, the value of I_{DS} decreases. Figure 4(b) shows the variation of I_{DS} with RH values when $V_G = 0$ V and $V_{DS} = 5$ V. According to I_{DS}, RH value can be estimated. Therefore, the oxygen plasma treatment provides an effective method to realize sensitive humidity sensing. It is also found that oxygen plasma treatment enables the electrical performance revival of the degraded MoS_2 FET after exposure to air for three months without passivation. As shown in Fig. 5, the source-drain current of the MoS_2 FET expose to air (orange line) decreases comparing with the untreated MoS_2 FET (black line) because of the adsorption of oxygen or dust in the environment. The plasma treatment can effectively remove the adsorbates and recover the on-current. However, it is noted that the threshold voltage cannot be recovered to the original value, which means that the MoS_2 FET is p-type doped. As discussed above, it may be due to the generation of MoO_3.



(a)

(b)

Fig. 4 I_{DS} at different RH values: (a) as a function of V_{DS} when $V_G = 0$ V; (b) when $V_G = 0$ V and $V_{DS} = 5$ V

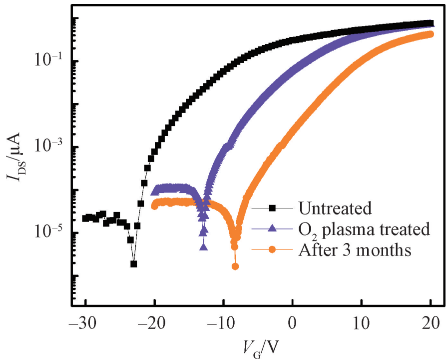


Fig. 5 Variation of transfer curves of MoS_2 FET at $V_{DS} = 0.1$ V under different conditions: untreated, oxygen plasma treated, and after three months of storage in humid environment (RH of 20%)

3 Conclusions

In conclusion, experiments were done to study the p-type doping effect of oxygen plasma on the electrical characteristics of multilayer MoS_2 FETs. The threshold voltage could be effectively tuned from −12 V to −2 V, while maintaining comparable charge carrier mobility, which was essential for reducing energy consumption required for practical electronic FETs. The Raman spectroscopy measurement further confirmed that the doping effect was attributed to the formation of MoO_3-like defects upon exposure to oxygen plasma. The humidity-sensing property of the plasma treated MoS_2 FET was also studied. The output curves showed an obvious saturation and the source-drain current value decreased with a change of approximately 54% in humid environment, which was attributed to plasma-induced adsorption centers for water molecules. The relationship between the current and different RH values was further presented. This work provides a simple approach for surface doping of 2D materials and makes a significant step towards transistor-based sensing applications.

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氧等离子处理的二硫化钼场效应晶体管表面掺杂和湿度传感研究

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东华大学 理学院，上海 201620

摘　要：二维半导体过渡金属二硫属化物（transition metal dichalcogenide，TMD）具有独特的电学、光学和力学性能，在数字电路、光伏器件和能量存储等多个领域中具有巨大的应用潜力。通过表面掺杂控制 TMD 的电学性能为实现灵敏传感提供了有效的方法。本文开展了氧等离子体对二硫化钼（MoS_2）掺杂特性的研究。首先，测试了 MoS_2 场效应晶体管（field-effect transistor，FET）的输运特性，发现氧等离子体处理对 FET 具有 p 型掺杂作用。随后，通过拉曼光谱研究了掺杂机制的成因，并证实了沟道表面类 MoO_3 缺陷的形成。最后，研究了经等离子体处理的晶体管的湿度传感特性，由于氧等离子体处理使得沟道对水分子的吸收中心增加，在潮湿环境下晶体管具有十分灵敏的响应特性，源漏电流值变化了约 54%。这项工作不仅提供了一种调控 TMD 电学性能的简单方法，也展示了低维材料化学传感器的发展潜力。

关键词：场效应晶体管（FET）；二硫化钼（MoS_2）；氧等离子体；表面掺杂；湿度传感