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Oxygen environmental and passivation effects on molybdenum disulfide field effect transistors

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Abstract
We investigated the effects of passivation on the electrical characteristics of molybdenum disulfide (MoS_2) field effect transistors (FETs) under nitrogen, vacuum, and oxygen environments. When the MoS_2 FETs were exposed to oxygen, the on-current decreased and the threshold voltage shifted in the positive gate bias direction as a result of electrons being trapped by the adsorbed oxygen at the MoS_2 surface. In contrast, the electrical properties of the MoS_2 FETs changed only slightly in the different environments when a passivation layer was created using polymethyl methacrylate (PMMA). Specifically, the carrier concentration of unpassivated devices was reduced to 6.5×10^{15} cm^{-2} in oxygen from 16.3×10^{15} cm^{-2} in nitrogen environment. However, in PMMA-passivated devices, the carrier concentration remained nearly unchanged in the range of 1–3×10^{15} cm^{-2} regardless of the environment. Our study suggests that surface passivation is important for MoS_2-based electronic devices.

S Online supplementary data available from stacks.iop.org/Nano/24/095202/mmedia

(Some figures may appear in colour only in the online journal)

1. Introduction

Two-dimensional (2D) nano-sheets acting as ultrathin active device films have gained significant interest for use in the miniaturization of electronic devices to the atomic-layer-thick level. For example, graphene has become an important material for atomic-layer electronic device applications due to its numerous advantages, such as high charge mobility, transparency, mechanical strength, and flexibility [1–4]. However, graphene cannot be used as an active channel in field effect transistors (FETs) because it either does not have a bandgap or has a narrow bandgap at best [5]. Numerous studies have been conducted to achieve a sufficiently wide bandgap in graphene nanostructures; however, the electrical properties of graphene are often degraded in the process. For example, graphene fabricated as a nano-ribbon has a bandgap of approximately 200 meV; however, its mobility is decreased by an order of magnitude compared to graphene sheets due to edge scattering [6, 7].

Recently, molybdenum disulfide (MoS_2), which is a transition-metal dichalcogenide semiconductor, has gained a significant amount of attention because it can also be formed as an atomic-layer-thick device and, more importantly, it has a bandgap. MoS_2 has a layered structure with S–Mo–S units bonded by van der Waals forces [8–11], so the mechanical exfoliation method can be applied to peel off individual layers [12]. Electrically, MoS_2 has an intrinsic indirect bandgap of approximately 1.2 eV in bulk form and a direct bandgap of approximately 1.8 eV as a single-layer [13, 14]. MoS_2 FETs have been reported to exhibit a high on/off current ratio of 10^6–10^8 and a low subthreshold swing value of 74 mV/decade [15]. Due to these semiconducting

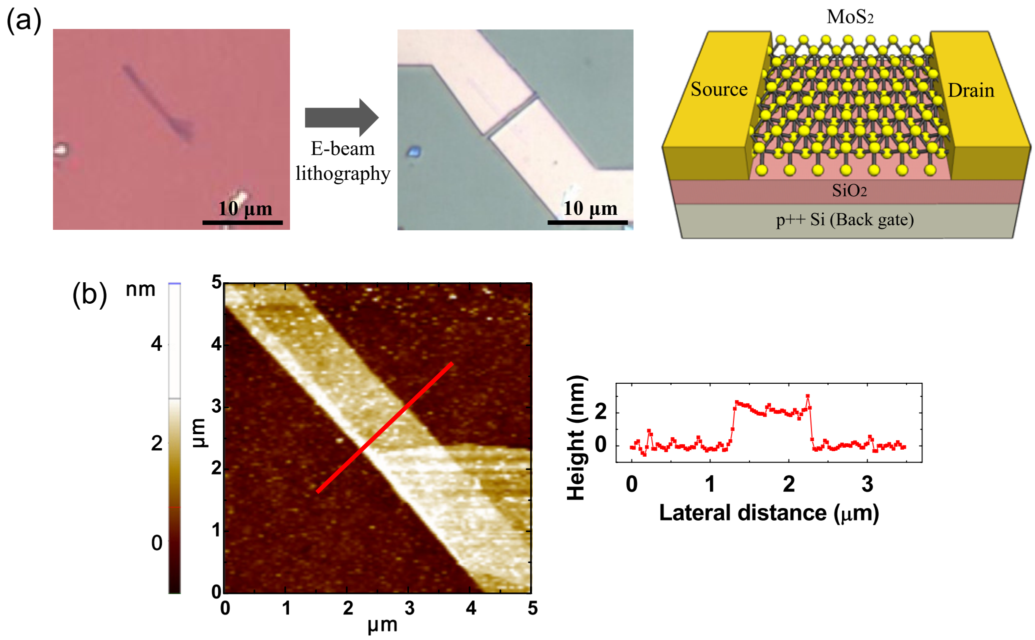

Figure 1. (a) Optical images of a MoS_2 nano-sheet on SiO_2 before (left) and after (middle) deposition of electrodes and a schematic of a MoS_2 FET (right). The channel length and channel width of this device are both approximately 1 μm. (b) AFM image (5 μm $\times$ 5 μm) of a 2 nm-thick MoS_2 nano-sheet deposited by micro-mechanical exfoliation onto 270 nm-thick SiO_2 (left) and a topographic cross-sectional profile across the line indicated in the AFM image (right).

properties of MoS_2, many studies have been conducted on electronic devices and circuits based on MoS_2 FETs [16–18]. Meanwhile, semiconductor surfaces are strongly influenced by the chemical adsorption of oxygen gases in ambient. Similarly, the electrical properties of semiconducting films, including MoS_2, are significantly affected by the chemical adsorption of ambient gases, mainly oxygen [19]. Therefore, MoS_2 FET devices should be carefully studied in different environments, and protection achieved through passivation should be considered to ensure consistent characteristics of the devices by minimizing the influence of the environment.

Here, we report on a detailed study of the effects of passivation on MoS_2 FETs under nitrogen, vacuum, and oxygen environments. The FET devices were fabricated with a few layers of MoS_2 films prepared by a mechanical exfoliation method on Si substrates. The MoS_2 FET devices were passivated with a polymethyl methacrylate (PMMA) layer, and the electrical properties of the MoS_2 FETs were investigated and compared before and after the PMMA passivation in different environments.

2. Experimental details

Bulk MoS_2 has a stacked structure of weakly bonded layers with van der Waals forces between the layers. Therefore, single-layer MoS_2 can be formed by exfoliating MoS_2 crystals in a manner similar to that of graphene. Several methods have been reported for MoS_2 exfoliation, including liquid phase exfoliation processing [20] and micro-mechanical exfoliation with Scotch tape. In our study, atomic layers of MoS_2 were prepared with the Scotch tape exfoliation technique. Figure 1(a) illustrates the fabrication of the MoS_2 FET devices. The exfoliated MoS_2 nano-sheets were formed on a Si wafer composed of 270 nm-thick SiO_2 on a highly doped p^{++} Si as a back gate (figure 1(a), left). After the positions of the MoS_2 nano-sheets were established using an optical microscope, the electrodes were patterned by electron-beam lithography (figure 1(a), middle). Then, to fabricate the MoS_2 FETs, Au (30 nm-thick) and Ti (10 nm-thick) were deposited and defined as the source and drain electrodes. The rightmost image in figure 1(a) shows a schematic of the final MoS_2 FET device structure. The channel length and channel width of the device shown in the middle image of figure 1(a) were both approximately 1 μm, and the thickness of the MoS_2 nano-sheet in this figure, as measured by atomic force microscopy (AFM), was approximately 2 nm (figure 1(b)). This total thickness indicates that this particular MoS_2 nano-sheet is a tri-layer MoS_2 because the height of monolayer MoS_2 is 0.65 nm. Then, we investigated the electrical characteristics of the MoS_2 FET devices under nitrogen, vacuum, and oxygen environments. After measuring the as-prepared MoS_2 FETs, we passivated the surface of the MoS_2 FETs using PMMA. The PMMA-passivated MoS_2 FET devices were then characterized under the same environments. The electrical measurements of the MoS_2 FETs were conducted using both a probe station (JANIS Model ST-500) with a controllable environment and a semiconductor parameter analyzer (HP 4145B) at room temperature.

3. Results and discussion

3.1. Oxygen environmental effects on MoS_2 FET

Figure 2 presents the electrical characteristics of a MoS_2 FET before passivation measured in a vacuum of approximately

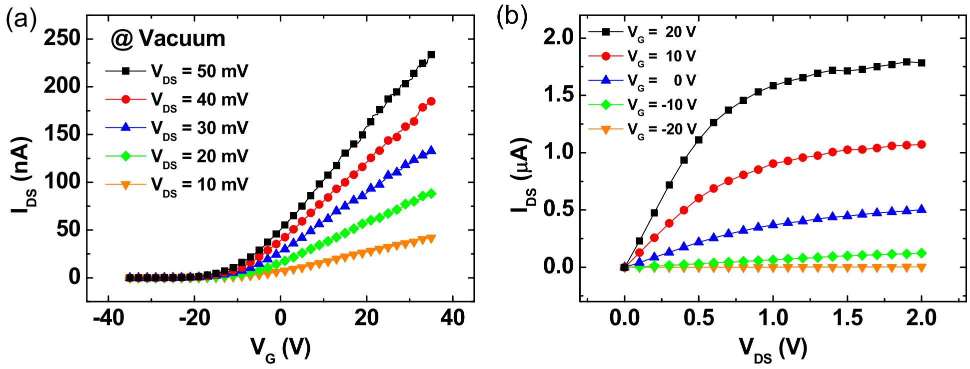

Figure 2. (a) I_{DS}–V_G characteristics and (b) I_{DS}–V_{DS} characteristics of an unpassivated MoS_2 FET measured in the vacuum environment.

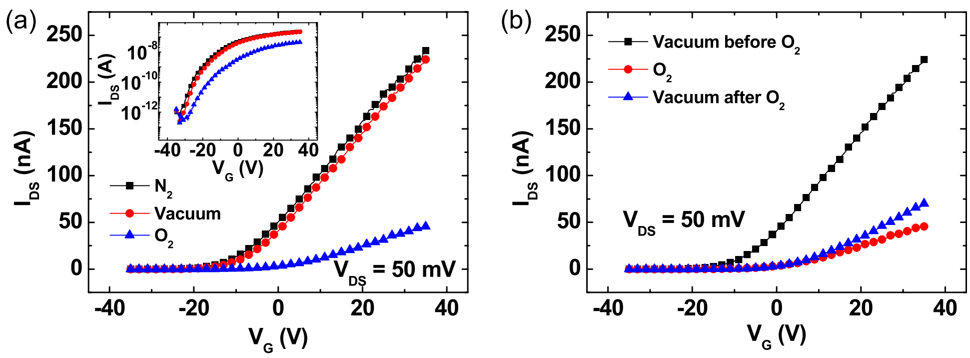

Figure 3. (a) I_{DS}–V_G characteristics of an unpassivated MoS_2 FET in the N_2, vacuum, and O_2 environments. The inset shows a semilogarithmic plot. (b) I_{DS}–V_G characteristics of the same device measured before and after exposure to O_2.

10^{-3} Torr. Figure 2(a) presents the transfer characteristics (source–drain current versus gate voltage, I_{DS}–V_G) for different source–drain voltages at a fixed source–drain voltage (V_{DS}) = 50 mV, and figure 2(b) displays the output characteristics (source–drain current versus source–drain voltage, I_{DS}–V_{DS}) for different gate voltages. The devices exhibited n-channel FET behavior because the positive gate voltages increased the current.

Figure 3(a) shows the I_{DS}–V_G characteristics of a MoS_2 FET in the nitrogen (N_2), vacuum, and oxygen (O_2) environments. A semilogarithmic plot is presented in the inset of this figure. The device measurements were conducted in a N_2 environment, followed by vacuum, and then an O_2 environment. The N_2 and O_2 pressure was set at 760 Torr (1 atm), and the vacuum pressure was set at 10^{-3} Torr. The current level of the device was similar in the N_2 and vacuum environments. However, in the O_2 environment, the current level was substantially reduced and the threshold voltage shifted in the positive gate voltage direction. This type of behavior, which has been previously reported for MoS_2-related FET devices in O_2 environments [19], is due to the absorption of oxygen molecules into sulfur or defect sites on the MoS_2 surface, which traps electrons and thus reduces the current of the MoS_2 FET [22]. Figure 3(b) displays the characteristics of the MoS_2 FET (the same device shown in figure 3(a)) before and after exposure to oxygen. The device was first measured in the vacuum environment ('vacuum before O_2'). The device was exposed to the O_2 environment and measured again, and then the O_2 was evacuated and the device was measured again in vacuum ('vacuum after O_2'). Similar to the data shown in figure 3(a), O_2 exposure reduced the current level compared to the current level in the vacuum. When the vacuum was reintroduced after O_2 exposure, the device did not recover to the original current level exhibited in the vacuum environment before the O_2 exposure. This observation indicates that the adsorbed oxygen molecules are not fully desorbed from the MoS_2 surface by a simple evacuation. In this case, thermal annealing may facilitate oxygen desorption [19]. We observed that the current could be recovered when the O_2-exposed devices were thermally annealed at 350 K in the vacuum environment (see figure S1 in the supporting information available at stacks.iop.org/Nano/24/095202/mmedia).

3.2. Passivation effects on MoS_2 FETs

The MoS_2 FET is sensitive to the environment, particularly the O_2 environment. Therefore, the MoS_2 FET should be protected against oxygen to maintain consistent device characteristics. One simple method for this purpose is to passivate the devices with a protective layer. In this study, we used PMMA passivation over the MoS_2 FET devices. The PMMA (950 PMMA 5% in Anisole) was spin-coated over the devices at a rate of 4000 rpm for 50 s (for a thickness of approximately 260 nm). Figure 4(a) shows the I_{DS}–V_G characteristics of a PMMA-passivated MoS_2 FET in

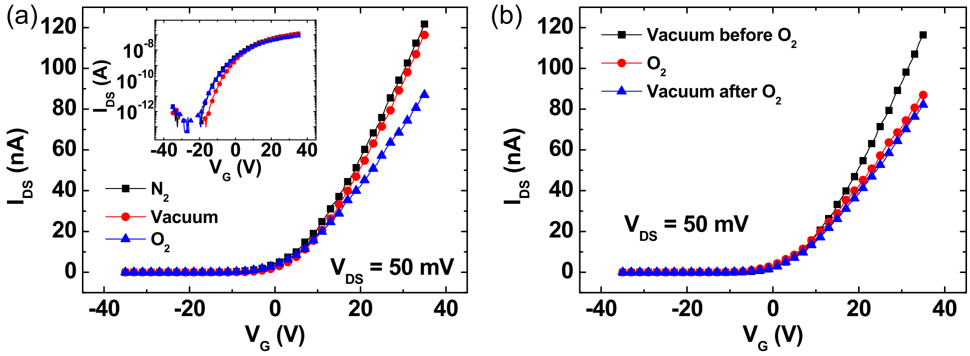

Figure 4. (a) I_{DS}–V_G characteristics of a PMMA-passivated MoS_2 FET in the N_2, vacuum, and O_2 environments. The inset shows a semilogarithmic plot. (b) I_{DS}–V_G characteristics of the same device measured before and after exposure to O_2.

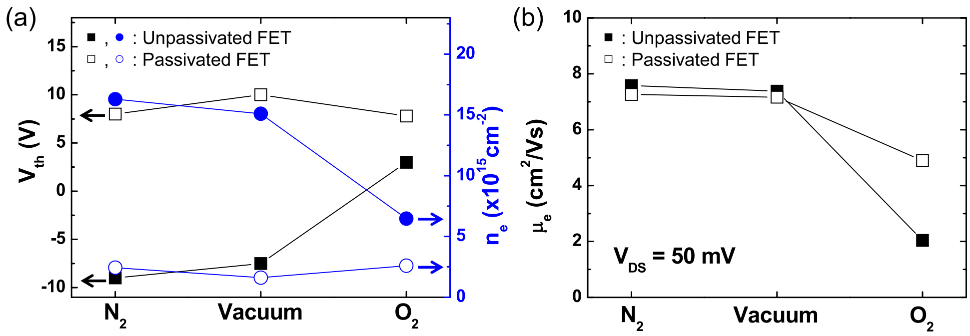

Figure 5. (a) Threshold voltage V_{th} and carrier density n_e and (b) carrier mobility μ_e for unpassivated and passivated MoS_2 FETs in the N_2, vacuum, and O_2 environments.

the different environments. We measured this device under the same measurement conditions used for the device shown in figure 3(a). The current levels of the PMMA-passivated device measured in the N_2 and vacuum environments were similar, consistent with the results for the unpassivated device (figure 3(a)). However, the device characteristics of the unpassivated and passivated devices after O_2 exposure were dramatically different. As shown in figure 4(a), the current level was also reduced after O_2 exposure but to a lesser extent than in the unpassivated device (figure 3(a)). The current reduction was roughly 80.4% and 28.5% for the unpassivated device and passivated device, respectively, with respect to the original current level measured in the N_2 environment. Figure 4(b) shows the characteristics of this PMMA-passivated MoS_2 FET (the same device shown in figure 4(a)) before and after exposure to O_2. The measurement conditions were the same as those for the unpassivated device (figure 3(b)). For the passivated devices, O_2 exposure also reduced the current level, but the reduction was not as significant as for the unpassivated device. The current did not fully recover when the O_2 was evacuated. These results indicate that PMMA was able to passivate the MoS_2 FET devices but that the passivation effect was not perfect. Note that the passivation effect was dependent on the PMMA preparation. The results in figure 4 were obtained after thermal annealing of spin-coated PMMA at 120 °C for 30 min on a hot plate. When the PMMA was not thermally annealed, the passivation effect was less efficient [21] (see figure S2 in the supporting information available at stacks.iop.org/Nano/24/095202/mmedia).

3.3. Electrical parameters of MoS_2 FETs before and after passivation

The threshold voltage can be defined as the gate voltage obtained by extrapolating the linear portion of the I_{DS}–V_G curve from the point of maximum slope to a zero drain current, where the point of maximum slope is the point at which the transconductance (dI_{DS}/dV_G) is at a maximum [22]. Before passivation (figure 3(a)), the threshold voltage of the MoS_2 FET shifted from −9 V in the N_2 environment to 3 V in the O_2 environment in the positive gate bias direction because more electrons were trapped by the oxygen than the nitrogen. As a result, electrons were depleted and the electron density in the MoS_2 FET decreased when the FET was exposed to the O_2 environment. Because the carrier concentration decreased after exposure to O_2, a higher positive gate bias was required to produce a current flow in the MoS_2 channel, and thus, the threshold voltage shifted in the positive gate bias direction. In contrast, when the MoS_2 FET was passivated with PMMA, the threshold voltages were 8 V in the N_2 environment and shifted only slightly to 7.8 V in the O_2 environment (figure 4(a)). The threshold voltages for the unpassivated and passivated MoS_2 FETs under different environments are summarized in figure 5(a).

The threshold voltages can be used to obtain the carrier concentration from the total charge, $Q_{total} = C_g|V_G - V_{th}|$, where C_g is the gate capacitance and V_{th} is the threshold voltage. The gate capacitance can be estimated by a parallel plate capacitor model. The carrier concentration n_e (total charge per area) was determined for a gate bias of 11 V for the MoS_2 FETs in the N_2, vacuum, and O_2 environments before and after PMMA passivation, and the values are summarized in figure 5(a). Here, 11 V was arbitrarily chosen because the MoS_2 FET is in the on-current state for all cases at this voltage (figures 3 and 4). Before passivation, the carrier concentration in the MoS_2 FET was estimated to be 16.3×10^{15} cm^{-2} and 15.1×10^{15} cm^{-2} in the N_2 and vacuum environments, respectively, and it decreased to 6.5×10^{15} cm^{-2} when the FET was exposed to the O_2 environment. As explained above, this observation is due to the fact that more electrons were captured by the oxygen molecules in the O_2 environment. However, after passivation, the carrier concentration remained nearly unchanged in the range of 1–3×10^{15} cm^{-2} regardless of the environment. The carrier mobility of the MoS_2 FET is plotted in figure 5(b). The carrier mobility μ_e in the low field region can be calculated by

$$\mu_e = \frac{dI_{DS}}{dV_G}\frac{L}{WC_iV_{DS}}, \tag{1}$$

where C_i is the capacitance between the channel and the back gate per unit area (i.e. $C_i = C_g/(LW) = \varepsilon_0\varepsilon_r/d \sim 1.3 \times 10^{-4}$ F m^{-2}), L, W are the channel length and channel width (both ~ 1 μm), respectively, and $V_{DS} = 50$ mV. Through this calculation, we obtained μ_e values of 7.6 cm^2 V^{-1} s^{-1} (N_2), 7.4 cm^2 V^{-1} s^{-1} (vacuum), and 2.1 cm^2 V^{-1} s^{-1} (O_2) before passivation and 7.3 cm^2 V^{-1} s^{-1} (N_2), 7.2 cm^2 V^{-1} s^{-1} (vacuum), and 4.9 cm^2 V^{-1} s^{-1} (O_2) after passivation. The carrier mobility of the MoS_2 FETs improved slightly after passivation.

4. Conclusions

In summary, we fabricated MoS_2 FET devices and characterized their electrical properties in N_2, vacuum, and O_2 environments before and after PMMA passivation. In the O_2 environment, the unpassivated MoS_2 FETs were significantly degraded in terms of current level, carrier concentration, and carrier mobility. However, the PMMA-passivated MoS_2 FETs maintained their device characteristics in different environments despite the fact that the passivation effect was not perfect. This study emphasizes the importance of surface passivation in MoS_2-based electronic device applications.

Acknowledgments

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Supporting Information

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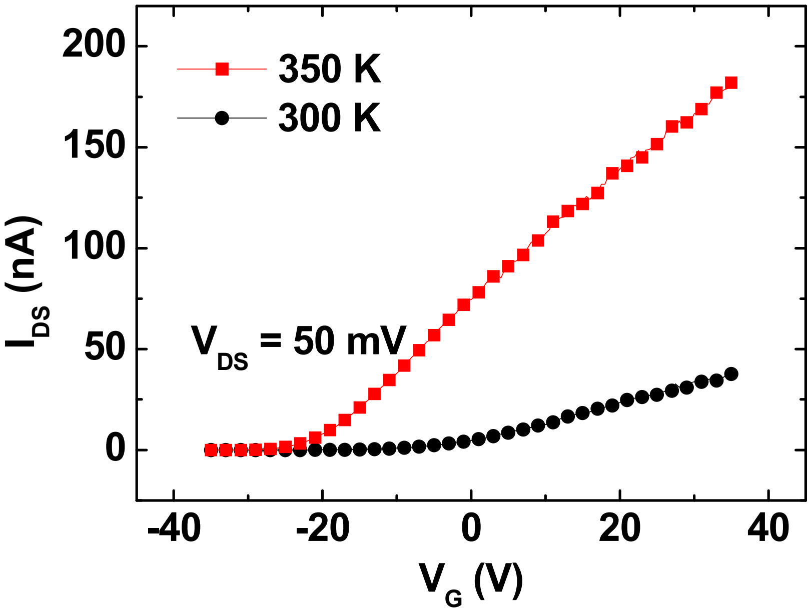

Figure S1. I_{DS}-V_G characteristics of a MoS_2 FET measured in vacuum at room temperature and at 350 K.

Figure S1 is the I_{DS}-V_G characteristics of an unpassivated MoS_2 FET measured at 300 K and 350 K in vacuum (~10^{-3} torr) after the device was exposed to oxygen. The current level was decreased significantly due to the oxygen environmental effect (see Figure 3 in the main manuscript). When the oxygen was simply evacuated and the device was measured in vacuum, the current was not recovered to the original current level (the curve measured at 300 K shown in Figure S1). This means that the adsorbed oxygen molecules are not fully desorbed from the MoS_2 surface by a simple evacuation. However, a thermal annealing can help the oxygen desorption [S1]. When the devices were thermally annealed at 350 K in vacuum, the current was recovered to ~80% of the original current level (Figure S1 and Figure 3).

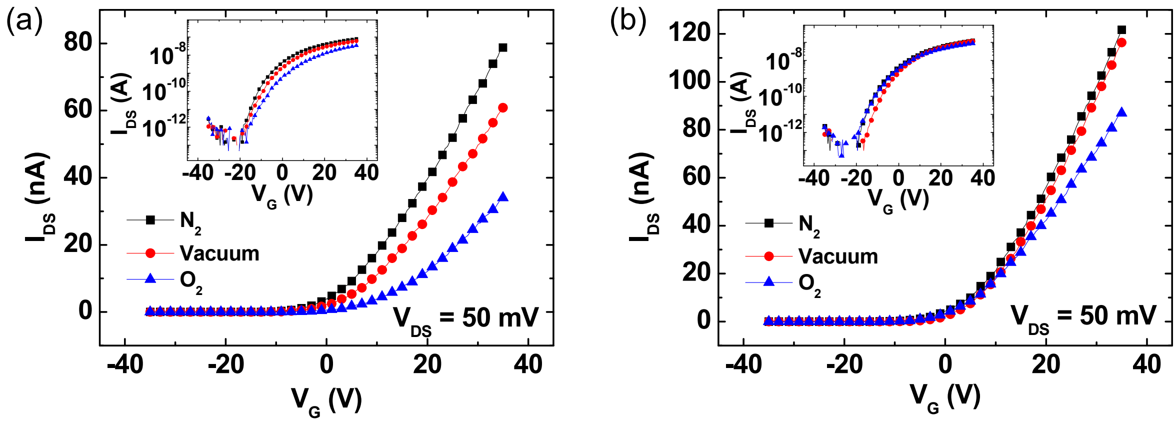

Figure S2. (a) I_{DS}-V_G characteristics of a PMMA-passivated MoS_2 FET measured in different environments. In this case, the PMMA-passivated device was not thermally annealed. (b) I_{DS}-V_G characteristics of another PMMA-passivated MoS_2 FET measured in different environments. In this case, the PMMA-passivated device was annealed at 120 ^{o}C for 30 min.

The electrical characteristics of PMMA-passivated MoS_2 FETs were measured without and with thermal annealing after PMMA spin-coating. Figure S2(a) shows a PMMA-passivated device without thermal annealing and Figure S2(b) shows a PMMA-passivated device with thermal annealing at 120 ^{o}C for 30 min. The bond strength of PMMA depends on temperature [S2]. In the case of unannealed PMMA (Figure S2(a)), the current level of the device was decreased dramatically in oxygen environment. This is because oxygen can penetrate the weakly-bond PMMA and can be adsorbed on the surface of MoS_2. Then, the oxygen causes electron trapping and consequently the current decreases. On the other hand, in the case of annealed PMMA (Figure S2 (b)), the current level was only slightly decreased in oxygen environment, and the characteristics of the device was almost independent of different environments. This is because the annealed PMMA forms strong bond, and therefore the annealed PMMA more effectively protected the MoS_2 FET against the oxygen molecules.

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