Tuning the electrical property via defect engineering of single layer MoS2 by oxygen plasma†

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We have demonstrated that the electrical property of single-layer molybdenum disulfide (MoS2) can be significantly tuned from the semiconducting to the insulating regime via controlled exposure to oxygen plasma. The mobility, on-current and resistance of single-layer MoS2 devices were varied by up to four orders of magnitude by controlling the plasma exposure time. Raman spectroscopy, X-ray photoelectron spectroscopy and density functional theory studies suggest that the significant variation of electronic properties is caused by the creation of insulating MoO3-rich disordered domains in the MoS2 sheet upon oxygen plasma exposure, leading to an exponential variation of resistance and mobility as a function of plasma exposure time. The resistance variation calculated using an effective medium model is in excellent agreement with the measurements. The simple approach described here can be used for the fabrication of tunable two-dimensional nanodevices based on MoS2 and other transition metal dichalcogenides.

Introduction

The discovery of graphene, by mechanical exfoliation from a layered bulk solid to a single atomic layer, and its extraordinary mechanical, electrical and optical properties have stimulated significant interest in other two dimensional (2D) materials and their heterostructures.1–4 A unique aspect of 2D materials is that they can exist with various intrinsic electronic properties such as metal, semimetal, semiconductor or insulator, which is defined by their coordination chemistry.5 Among the different 2D materials, graphene (semimetal) and molybdenum disulfide (semiconductor) have been receiving the most attention. While graphene has very high mobility, the lack of a bandgap in its electronic structure limits its application in nanoelectronics and optical devices. On the other hand, MoS2, a member of the transition metal dichalcogenides (TMDC) family, offers a layer-dependent electronic bandgap: bulk MoS2 is an indirect bandgap material with a gap of 1.2 eV which transitions into a direct bandgap of 1.8 eV in a single layer MoS2.8 As a result, field effect transistors (FETs) based on single-layer MoS2 have shown a current switching of up to 108 [ref. 9] in addition, it was shown that the mobility of the MoS2 FETs is also layer dependent: it increases with the number of layers up to 10 layers and then decreases for higher thicknesses.19 Consequently, single and multi-layer MoS2 have been extensively studied and hold great promise for future applications in nano-electronic devices. In fact, several prototype devices based on single and multilayer MoS2 such as phototransistors, chemical sensors, photovoltaic devices, diodes, memory devices and integrated circuits, have already been demonstrated.8–19

Electrical and optical property variations have been observed with the number of layers, however, a more recent effort has been focused on engineering the material properties of the single layer MoS2 by an external control. The grand challenge is to determine whether the metal, semiconductor, and insulator ‘phases’ can be realized in the same 2D material using an external control without resorting to multiple 2D materials. Since the 2D materials are atomically thin, their electronic and optical properties are highly sensitive to the external control. For example, metallic behavior has been found in lithium intercalated single-layer MoS2.20 A theoretical study predicts that, owing to its lower symmetry, strain engineering can be used to tune the MoS2 bandgap, which can in turn modulate electrical and optical properties. For example, it was predicted that a transition from a direct to an indirect bandgap can be achieved in single-layer MoS2 by strain engineering.21–23 Recent experiments have suggested that electronic structure
modification is indeed possible by strain engineering, however experimental evidence of the electrical property tunability using such a technique is still lacking. The ability to continuously modulate electronic properties in the same layer will enable the fabrication of nano-devices with a wide range of tunability of electronic and optical properties.

Here, we demonstrated a novel approach to continuously tune the electrical properties of a single-layer MoS₂ FET from the semiconductor to the insulator using an external control. The approach presented here is based on the controlled exposure of MoS₂ to oxygen plasma (an O₂–Ar mixture of 20 : 80) for different exposure times. We show that the mobility, on-current and resistance of a single-layer MoS₂ FET vary exponentially by up to four orders of magnitude with respect to the plasma exposure time. Raman studies conducted before and after plasma treatment show a significant decrease in the intensity of MoS₂ peaks with the creation of a new oxidation induced peak, while the X-ray photoelectron spectroscopy (XPS) study shows peaks associated with MoO₃ after the plasma exposure. We suggest that during the exposure to oxygen plasma, the energetic oxygen molecules interact with MoS₂ and create MoO₃-rich defect regions, which are insulating. The coverage of the defect regions increases with the exposure time. This result is confirmed by density functional theory (DFT) calculations. We have also used a theoretical model based on effective medium approximation to describe the resistance as a function of plasma exposure time. Our results show that the effective medium semiconductor (EMSC) made of MoS₂ including MoO₃ defect regions acts as a tunnel barrier for the injected conduction electrons, giving rise to the exponential increase in resistivity as a function of plasma exposure time, which is in excellent agreement with our experimental data. Our calculations demonstrate an increase in the tunnel barrier height of 0.06 eV for each second of the plasma exposure time. Our findings suggest a simple and efficient approach for the in-plane engineering of electrical properties of MoS₂ which can be applied to other TMDCs as well and will enable the fabrication of a wide range of tunable 2D nanodevices.

Experimental section

Device fabrication

The devices were fabricated using single layers that were mechanically exfoliated from a commercially available crystal of molybdenite (SPI Supplies Brand, Natural Molybdenite) using the adhesive tape micromechanical cleavage technique and deposited on a highly doped Si substrate capped with a thermally grown 250 nm thick SiO₂. Before MoS₂ deposition, the Si/SiO₂ wafers were cleaned using oxygen plasma followed by rinsing with acetone and isopropyl alcohol. Standard electron beam lithography (EBL) was used to pattern metal contacts on the MoS₂ flakes. First, a double-layer electron beam resist, methyl methacrylate/poly(methyl methacrylate) (MMA/PMMA), was spun on the substrate and baked, followed by the e-beam exposure and development in (1 : 3) methyl isobutyl ketone : isopropyl alcohol (MIBK : IPA). After defining the electrodes, 35 nm Au was deposited by thermal evaporation, followed by lift-off in acetone.

Electrical transport measurements

The electron transport measurements of the MoS₂ device were performed on a probe station at ambient conditions using a Keithley 2400 source meter and a DL instruments 1211 current preamplifier interfaced with LabView program. The measurements were performed for the pristine flake and after each oxygen plasma treatment. The plasma treatment on the MoS₂ devices was carried out using a commercial (Plasma Etch, PE-50) plasma chamber at a power of 100 W operating at 50 kHz. During plasma exposure, the pressure within the plasma chamber was held at 250–350 mTorr and a gas mixture of oxygen (20%) and argon (80%) was passed at a constant rate of 15 sccm. For the first exposure, the samples were exposed for 2 s, and subsequently they were exposed at 1 s intervals and the electron transport measurements were repeated.

Characterization

XPS was performed to analyze any possible change in the chemical composition of MoS₂ flakes due to plasma treatment on a Physical Electronics 5400 ESCA system utilizing a monochromatized Al Kα X-ray source. MoS₂ flakes containing both single layer and multi-layer were exfoliated on a SiO₂ substrate and XPS was carried out both before and after the plasma exposure. Raman spectra of the as-exfoliated and plasma-treated MoS₂ flakes were recorded with a Witec alpha300RA confocal Raman system. The MoS₂ flakes were illuminated with 532 nm laser light in the ambient air environment at room temperature. The power of the laser line was kept below 1 mW in order to avoid any damage to the flake, while maintaining a good signal to noise ratio.

Theoretical calculations

Density functional theory calculations (DFT) were performed to investigate the stability of MoOS and MoO₃ defects inside a single layer of MoS₂. For that, we performed DFT calculations for a single layer of MoS₂, a single layer of MoO₃, a single layer of MoS₂ with MoOS defects and a single layer of MoS₂ with MoO₃ defects. In each of these cases we considered a mesh of 9 × 9 × 1 k-points in the Brillouin zone. The ion-electron interaction is described by the projected augmented wave (PAW) method and the exchange-correlation energy is calculated using the Perdew–Burke–Ernzerhof (PBE) approximation within the framework of the generalized gradient approximation (GGA). The grid point cutoff of 415 eV is used, and a maximum force of 0.1 eV Å⁻¹ on each atom is reached during the optimization process in all cases.

Results and discussion

Fig. 1(a) shows an optical micrograph and Fig. 1(b) shows an atomic force microscopy (AFM) topographic image of a representative single-layer flake on a Si/SiO₂ substrate. The height profile of a flake shown in Fig. 1(b) indicates a thickness of

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0.9 nm, corresponding to a single layer. The number of MoS2 layers was further confirmed by Raman spectroscopy performed before making electrical contacts to the flake, as shown in Fig. 1(c). Two prominent peaks at 2E2g and A1g corresponding to in-plane and out-of-plane vibrations of Mo and S atoms were separated by a Raman position difference \( \Delta = 19.28 \, \text{cm}^{-1} \), confirming the single layer nature of the flake. Standard electron beam lithography (EBL) was used to pattern Au contacts on the MoS2 flakes. An optical micrograph of a representative fabricated device is shown in the inset of Fig. 1(e).

Fig. 1(d) shows the output characteristics \( (I_D) \) for different back-gate voltages \( (V_G) \) ranging from –60 to 40 V (bottom to top) with a step of 10 V. The increase of drain current with the gate voltage indicates n-type FET behavior. The asymmetric behavior (a higher current at positive bias) suggests that a small Schottky barrier is present at the contact. Fig. 1(e) shows the transfer characteristics (drain–current \( I_D \)) as a function of back-gate voltage \( V_G \) measured at a fixed source–drain bias voltage \( V_{DS} = 100 \text{ mV} \) for the pristine MoS2 device. The \( I_D \) increased by several orders of magnitude with the increase of \( V_G \). The current on-off ratio of the device is found to be \( \sim 10^4 \). The field effect mobility of the device was calculated to be 6 cm² V⁻¹ s⁻¹ using the relation \( \mu = \frac{L}{W(C_{Ox}V_{DS})} \left( \frac{dI_D}{dV_G} \right) \), where \( L \) is the channel length, \( W \) is the channel width and \( C_{Ox} = \varepsilon_0\varepsilon_r\varepsilon_0/d \) is the capacitance between the gate and SiO2, with \( \varepsilon_r \sim 3.9\varepsilon_0 \) is the effective dielectric constant of SiO2, and \( d (=250 \, \text{nm}) \) is the oxide thickness.

Fig. 2(a) shows the transfer characteristics of the same device after different plasma exposure times. For a unified view of the curves, we multiplied the curve for the 0 s (pristine MoS2) exposure by 0.01 and 2 s exposure by 0.5. Interestingly, the drain current at all gate voltages decreases with increasing oxygen plasma exposure. This can be more clearly seen in Fig. 2(b) (right axis) where the on-current at \( V_G = 40 \text{ V} \) is displayed in a semi-log scale. The drain current was \( \sim 285 \text{ nA} \) for the as-fabricated sample, which decreased exponentially with time to a value of less than 20 pA, a drop of more than four orders of magnitude, after only a total of 6 s plasma exposure time. After the 6 s exposure, the current becomes negligibly small. The mobility of the device after each plasma exposure is calculated from the \( I_D \) – \( V_G \) curves in Fig. 2(a), and is plotted in Fig. 2(b) (left axis) in a semi-log scale. Like the on-current, the mobility also drops exponentially from 6 cm² V⁻¹ s⁻¹ for the as-fabricated sample to \( 4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) after the 6 s plasma exposure. Similar to on-current, the decrease of mobility is also more than four orders of magnitude with the plasma exposure.

Fig. 3(a) shows the \( I_D \) – \( V_{DS} \) graph of the device at \( V_G = 40 \text{ V} \) for different plasma exposure times. It is observed that at all exposure times, the \( I_D \) – \( V_{DS} \) curves are linear around the zero bias representing the Ohmic behavior, from which we can measure the resistance. Fig. 3(b) demonstrates the dependence of resistance with respect to the plasma exposure time. The resistance increased by up to five orders of magnitude with increasing plasma exposure time. The logarithmic plot in Fig. 3(b) demonstrates that the resistance increases exponentially upon plasma exposure. Similar changes in the resistance were also observed for other gate voltages (see ESI S1†). This can be described by an effective medium model which shows that the exponential increase in the resistance in the function of plasma exposure time leads to the gradual increase of the tunnel barrier raised by the effective medium semiconductor.
(EMSC) material made of MoS₂ and strain-inducing MoO₃-rich defect regions.

Similar device characteristics were obtained on two other single layer devices (see ESI S2†). To explore the physical mechanism responsible for the observed change in electronic transport properties, we performed Raman spectroscopy and XPS on the pristine and plasma-treated MoS₂ flakes. Raman spectroscopy is a powerful tool to investigate changes in the composition of 2D materials. Here we compare the Raman signature of the pristine flake and the plasma-treated monolayer. Fig. 4(a) shows the Raman spectra of a representative single-layer MoS₂ flake before (red curve) and after 6 s of oxygen plasma treatment (green curve). The two Raman peaks corresponding to E₂g₁ (≈385 cm⁻¹) and A₁g (≈410 cm⁻¹) modes, characteristic of MoS₂ observed in the pristine flake, clearly decrease in amplitude after treatment. Interestingly, E₂g₁ (in plane) is severely affected as a result of the treatment, while A₁g shifts only by 3 cm⁻¹ with strong amplitude decrease (6 times) and a significant broadening. Finally, the disappearance of LAM mode at 450 cm⁻¹ also confirms the disruption of the MoS₂ lattice during the oxygen plasma treatment. On the other hand, the appearance of other peaks observed in the 150–400 cm⁻¹ range, particularly at 225 cm⁻¹ suggests an oxidation induced peak in the system. The XPS data presented below show the presence of a Mo⁶⁺ peak. Therefore, the observed oxidation induced peak in Raman data may indicate the formation of MoO₃.²⁶,²⁷

Fig. 4(b) shows the XPS spectra of pristine MoS₂ and plasma-treated MoS₂ respectively. Three prominent peaks were observed at energies 227 eV, 229.7 eV, and 233.1 eV in the pristine MoS₂ sample, the origin of which has been attributed to the binding energy of S 2s, Mo 3d₃/₂ and Mo 3d₅/₂ electrons in the Mo–S bond of the MoS₂ crystal, respectively.²⁶,²⁹ All these peaks were also found at the same binding energies for the plasma-treated sample, however an additional peak at energy 236.4 eV could be observed, corresponding to the higher oxidation state Mo⁶⁺ (ref. 29). Although, the XPS dataset is representative of all the flakes (from single layer to >20 layers) located in the probed region (around 2 μm for the XPS beam), as the beam size is much larger than the typical single-layer MoS₂ flake size, and flakes with different thicknesses are deposited on the substrate during mechanical exfoliation, the data show the possibility of MoO₃ formation under oxygen plasma. By calculating the areas under each peak, we could obtain a rough estimate for the fraction of MoO₃ present in the sample, which in this case was ~12%.

In previous experiments, oxygen and argon plasma were used on single-layer and multi-layered MoS₂ for etching purpose.¹⁸,³⁰,³¹ In order to ensure that the electrical property variation is not due to etching, we have acquired SEM images before and after the oxygen plasma treatment of a single-layer MoS₂ sample and found that the single layer was not etched after the 6 s plasma treatment (see ESI S3†). The difference with previous studies may be due to the process recipe. During the plasma process, the etching rate depends on the oxygen concentration, rf power, frequency and plasma exposure time.³²,³³ The previous experiments used either a high power reactive ion etcher or a significantly longer plasma exposure time. For example, Ar plasma was recently used for thinning of multilayer MoS₂.³¹ In that case, RF frequency was used and thinning was reported after 115 s of plasma exposure. In contrast, we used moderately low power and low frequency O₂–Ar plasma for a short duration [maximum 6 s]. Oxygen is a strong reactive element which can change the composition of surface molecules. This suggests that the changes in the electron transport property observed in the single-layer MoS₂ are due to oxygen plasma treatment and Mo–O based defect formation.

Based on the Raman and XPS studies, we propose the following qualitative picture to explain the electrical property evolution of MoS₂ during plasma treatment high energy charged particles bombard the MoS₂ surface. Since S atoms have a smaller mass compared to Mo, S atoms can move out of the lattice site and lattice vacancies are created. Because of the excess oxygen supplied by the plasma, oxidation takes place at the defect sites created by S vacancies on the surface.³⁴,³⁵

The oxidation process described as 2MoS₂ + 7O₂ → 2MoO₃ + 4SO₂,²⁷ MoO₃ has an experimentally measured bandgap of 3.2–3.8 eV, making it insulating in nature.³⁶ Therefore, the generation of MoO₃ in MoS₂ creates significant distortion of lattice (Fig. 5), which increases with increasing plasma exposure time. The resulting material can be treated as an EMSC which can explain the exponential variation of resistance (discussed later). The effect of MoO₃ defect regions on the transport properties of MoS₂ can be further studied at low temperature which will provide some important insights about the defect density, domain size, variable range hopping and localization lengths as has been done for 2D chemically-modified graphene.³⁷–⁴⁰

In the following we present our calculations based on density functional theory (DFT) as implemented in the atomistix tool kit (ATK) program (see Materials and methods). The most important fact that needs to be remembered is that a single layer of MoS₂ and a single layer of MoO₃ have completely different lattice structures. A 2D layer of MoS₂ has Mo atoms sandwiched between the S atoms with a honeycomb lattice structure as

![Fig. 4](image-url)
shown in Fig. 6(a). Two (0001) MoS2 layers bind weakly through van der Waals interaction, thus making mechanical exfoliation along the c direction possible. On the other hand, MoO3 has an orthorhombic layered structure with separate layers stacked along the b direction. A single sheet of MoO3 consists of bilayers with both sides terminated with O atoms, as shown in Fig. 6(b). The interlayer is bridged by the O atoms along the [100] direction. Due to the O atom termination of the single sheet of MoO3 on both sides, there is a weak van der Waals bond along the [001] direction in MoS2 and [010] direction in MoO3. Thus, the introduction of MoO3 defects in a single layer of MoS2 results in significant lattice distortions. Our results show that MoO3-rich defect regions can be created by introducing oxygen and that MoO3 defects are stable inside MoS2 (Fig. 6). We then replace three S atoms with three O atoms within a $2 \times 2$ supercell (doubling the lattice constant of the unit cell along the a and b directions). As O atoms form bonds with the Mo atom, the original plane of the S atoms is distorted. After optimization, it is evident that covalent bonds form between one of the Mo atoms (cyan) and the three O atoms, providing evidence for the stable configuration containing a MoO3 defect.

We also looked at the possibility of MoO$_2$ formation by optimizing the structure where two S atoms are replaced by two O atoms. DFT calculations show that MoO$_2$ defects can also exist. We note that, in the DFT calculations, we did not consider the effects of parameters such as temperature and kinetic...
energy of plasma, which may affect the outcome. However, due to the following reasons, we believe that MoO$_2$ may not be present in our experimental measurements: in XPS, the MoO$_2$ peak (Mo$^4+$) occurs at the binding energy of 229.2 eV, which overlaps with the 3d$_{5/2}$ peak of MoS$_2$ (229 eV). In addition, the O1s peak for MoO$_2$ overlaps with the MoO$_3$ peaks (MoO$_2$ is at 530.4 eV and MoO$_3$ at 530.6 eV). Therefore, it is difficult to identify MoO$_2$ in the presence of MoS$_2$ and MoO$_3$ using the Mo(3d) spectra. In any case, our electronic transport data present clear clues that MoO$_2$ may not be present in our sample. The presence of any MoO$_2$ defects inside MoS$_2$ would not increase the resistance exponentially because MoO$_2$ is not an insulator, but a metal.$^{1,4}$ However, our transport measurements show (see Fig. 2a and 3b) that there is an exponential increase in the resistance as a function of plasma exposure time. This indicates that the transport properties of our plasma-treated MoS$_2$ are mainly dominated by the MoO$_2$ defects which block the current flow as it has a higher bandgap than MoS$_2$ as discussed in our EMSC theory below. Therefore, we conclude that majority of the defects in a MoS$_2$ sheet are MoO$_2$. Further study such as an intensive computational calculation on molecular dynamics or real time simulation is required to rule out theoretically the possibility of the formation of MoO$_2$ defects.

The XPS and DFT analysis show evidence of the presence of MoO$_2$ defects along with their surrounding lattice distortions due to oxygen plasma. It is clear that the effect of the plasma treatment on the structure of the MoS$_2$ layer is not homogeneous, as it forms regions with variable concentrations of MoO$_3$ defect regions in MoS$_2$ and a complex network of heterojunctions that affect the electron transport (Fig. 6). For a qualitative description of the effect of such a complex network on resistance, we adopt the approximation of an effective medium, which regards the plasma-treated material as an EMSC (see ESI Fig. S4†). For simplicity, we assume the EMSC has a homogeneous structure whose work function depends on the plasma exposure time ($\tau$). Thus, we effectively have a heterostructure of EMSC – MoS$_2$. The electron transport through the EMSC – MoS$_2$ interface is determined by the respective band bending and the built-in potential $\Delta\phi(\tau)$, which depend on the concentration of defects and, therefore, depend on the plasma exposure time. It is natural to assume that with an increasing concentration of defects the built-in potential evolves towards its limiting value characterizing the MoS$_2$–MoO$_3$ interface ($\tau \to \infty$). Thus the maximal value of $\Delta\phi$ can be estimated using Anderson’s rule:

$$\Delta\phi_{\text{max}} = \phi_{\text{MoO}_2} - \phi_{\text{MoS}_2} \approx 2 \text{ eV},$$

where $\phi_{\text{MoS}_2} \approx 4.9$ eV (ref. 44) and $\phi_{\text{MoO}_2} \approx 6.9$ eV (ref. 45) are the respective work functions. The values of $\phi_{\text{MoS}_2}$ and $\phi_{\text{MoO}_2}$ reported in the literature vary noticeably, but in any case $\Delta\phi_{\text{max}} > 1 \text{ eV}$ can be expected. Such a strong built-in potential results in a great increase of resistance $R/\text{res} = \exp(\Delta\phi_{\text{max}}/k_B T) \sim 10^{12}$, where $k_B$ is the Boltzmann constant and $T$ is the temperature (see ESI† for details). This is well above the value of $\sim 10^4$ measured in the experiment and suggests that our final EMSC is not a crystalline MoO$_3$ sheet, in agreement with physical characterization. Rather, our experiment suggests that $\Delta\phi$ varies with the plasma exposure time and should have values: $0 \leq \Delta\phi(\tau) \ll \Delta\phi_{\text{max}}$. Taking this circumstance into account we can expand $\Delta\phi(\tau)$ in series with respect to $\tau$, and keeping only the linear term we present $\Delta\phi(\tau) = \alpha \tau$, where $\alpha$ is the rate at which the barrier increases. Thus we obtain

$$\ln\left(\frac{R(\tau)}{R(0)}\right) \sim \frac{\alpha \tau}{k_B T}$$

for the dependence of resistance on the plasma exposure time. It is interesting to note that the results obtained from this rather simple model are in excellent agreement with our experimental results shown in Fig. 3(b), with $\alpha \approx 6 \times 10^{-2}$ eV s$^{-1}$. This calculation also suggests that with longer oxygen plasma exposure, the work function of the exposed region increases. For the same reason, the mobility and on-current decrease with the plasma exposure time.

Conclusions

In conclusion, we report the electrical property tunability of single-layer MoS$_2$ devices upon controlled exposure to oxygen plasma. The on-current, mobility and resistance can be tuned by up to four orders of magnitude by varying the plasma exposure time. Based on our Raman spectroscopy, XPS, and DFT studies, we present strong evidence that the significant decrease of mobility and on-conductance is caused by the creation of insulating MoO$_3$-rich disordered domains, which cause significant lattice distortions in the MoS$_2$ sheet upon oxygen plasma exposure. Using a simple and effective medium model we show that the tunnel barrier of the plasma-treated MoS$_2$ increases at a rate of $\alpha \approx 6 \times 10^{-2}$ eV s$^{-1}$ with the plasma exposure time. The method for the electrical property tuning of MoS$_2$ devices described here can serve as an enabling technology for fabricating tunable 2D nanodevices for electronic and optoelectronic applications.

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