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Cite as: Appl. Phys. Lett. 114, 091103 (2019); https://doi.org/10.1063/1.5086726
Submitted: 22 December 2018. Accepted: 16 February 2019. Published Online: 04 March 2019

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Photoresponsivity enhancement in monolayer MoS$_2$ by rapid O$_2$:Ar plasma treatment

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ABSTRACT
We report up to ten-fold enhancement of the photoresponsivity of monolayer molybdenum disulfide (MoS$_2$) by treatment with O$_2$:Ar (1:3) plasma. We characterize the surface of plasma-exposed MoS$_2$ by TEM, Raman, and PL mapping and discuss the role of MoO$_x$ in improving the photocurrent generation in our devices. At the highest tested laser power of 0.1 mW, we find ten-fold enhancements to both the output current and carrier field-effect mobility at the illumination wavelength of 488 nm. We suggest that the improvement of electrical performance is due to the surface presence of MoO$_x$ resulting from the chemical conversion of MoS$_2$ by the oxygen-containing plasma. Our results highlight the beneficial role of plasma treatment as a fast and convenient way of improving the properties of synthetic 2D MoS$_2$ devices for future consideration in optoelectronics research.

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Two-dimensional layered transition metal dichalcogenides (TMDs) have attracted wide research interest due to their intriguing physical properties and potential applications. Molybdenum disulfide (MoS$_2$), a typical layered TMD, is a semiconductor with a direct bandgap of $\sim$1.8 eV in the single-layer limit. This allows monolayer MoS$_2$ field-effect transistors (FETs) to achieve high ON/OFF ratios and make them attractive candidates for switching components in future electronics. Recently, optoelectronic devices fabricated from MoS$_2$ have received notable attention. MoS$_2$ phototransistors are easy to fabricate, respond to a wide range of wavelengths, and exhibit fast DC photoresponses. In addition, their photoresponsivity can be tuned by various methods, such as back-gating, strain engineering, layer decoupling, and evaporation of sub-stoichiometric molybdenum oxide overlayers. Surface sensitization of monolayer MoS$_2$ FETs has also yielded significant enhancements of the measured photocurrent in the case of quantum dots, organic molecules, and metal nanostructures. However, these methods often involve additional preparation steps in order to fabricate the sensitizing species and deposit it on the MoS$_2$ device. Moreover, the surface-deposited dopants may not be robust to mechanical stressing or further material modification without losing their favorable properties.

Plasma functionalization, in turn, presents a fast and facile way to alter the crystal structure of on-chip layered materials such as MoS$_2$. It facilitates large-scale, multi-sample, and rapid tuning of the optoelectronic performance of FETs based on layered semiconductors. In particular, oxygen-containing plasmas tend to form sub-stoichiometric molybdenum oxides on the surface of MoS$_2$. These oxide centres can then act as dopants that alter the charge concentration in the modified MoS$_2$ transistor channel, and ultimately govern the electron conduction behavior of the newly formed oxide/MoS$_2$ heterostructure. In this work, we demonstrate the enhancement of the photoresponsivity of chemical vapour deposition (CVD)-grown monolayer MoS$_2$ by O$_2$:Ar (1:3) plasma treatment. The photoresponsivity is improved ten-fold in gated devices after 2 s of exposure to the plasma. At the same time, the field-effect mobility of the device under illumination improves by over one order of magnitude. We carry out transmission electron microscopy (TEM) imaging and spectroscopic mapping to characterize the sample after plasma exposure and...
attribute the observed photoresponse to the suppressed charge recombination mediated by surface-bound molybdenum oxides.

MoS\(_2\) samples were synthesized on SiO\(_2\)/Si substrates using the CVD method previously reported.\textsuperscript{28} The flake thickness was confirmed by optical microscopy and Raman spectroscopy. Standard EBL was carried out to fabricate the FET devices using PMMA resist and development in methyl isobutyl ketone/isopropanol (MIBK: IPA) (1:3). This was followed by metalization with Ti(10 nm)/Au(40 nm) contacts and lift-off in acetone. Plasma treatment was carried out on a Fischione Instruments 1020 cleaner for 2 s, utilizing O\(_2\):Ar (1:3) gas at a pressure of ∼5 mbar. The electrical testing was performed at room temperature in a two-probe configuration (Imina miBot) using a source meter unit (Agilent B2912A) in the ambient. The devices were back-gated through the heavily p-doped Si substrate underneath the 285 nm SiO\(_2\) overlayer. A 488 nm laser was used for irradiation. Its power density was tuned at five different levels and controlled to ensure no fluctuation throughout the experiment. The laser was directed through a condenser lens (20×, NA = 0.4), and the spot size was a1.5 μm. TEM was carried out on a FEI Titan 80–300 system operating at 300 kV. Monolayer samples were transferred onto copper grids using a polymer stamp. Fabricated devices were imaged using a Zeiss Nanofab helium ion microscope at a beam energy of 25 keV. Raman and photoluminescence (PL) spectra were acquired using a WITec Alpha 300R system (<100 μW) was used during mapping to minimize any laser-induced damage or heating of the sample.

The inset of Fig. 1(a) is a false-color helium ion micrograph of a typical contacted device. The contacts in our devices were always deposited in a parallel geometry, as visible in the image. The transistor channel length was over 5 μm to confine the laser irradiation solely to the MoS\(_2\) region. We collected the output and transfer characteristics of the device under 5 different illumination powers. As the laser spot avoided the Au electrodes during illumination, we assume that all of the measured photo-generated current originated from the MoS\(_2\) semiconductor. The measured photo-generated current originated from the MoS\(_2\) semiconductor.

Figure 1(a) shows the output characteristics of the device under laser illumination before any plasma treatment. Prior to any exposure to the plasma, the low-bias IV response of the MoS\(_2\) FET shows a well-behaved linear increase with applied bias for both voltage polarities, indicating good ohmic contacts to the semiconductor. Upon successive irradiations with rising laser power, the photocurrent increases, which is typical for semiconducting monolayer MoS\(_2\) devices.\textsuperscript{29–31} The output current reaches nearly 10 μA at ±5 V at the highest tested laser power of 72 μW. Figure 1(b) tracks the IV curves after 2 s of exposure to the plasma. We see that the current increases to nearly 25 μA at the highest illumination power, compared with the untreated sample at the same applied drain-source voltage. This indicates that dopants introduced by the plasma treatment to the MoS\(_2\) surface mediate an enhanced charge carrier photo-generation response in the device. We note that longer plasma treatments (>2 s) lead to a significant decay of electrical performance and do not enhance the photoresponsivity (see Fig. S2).

Figure 2(a) shows the transfer curves for the same sample before any plasma treatment. Our as-grown devices perform as standard n-type FETs with a field-effect mobility (\(\mu\)) of 0.13 cm\(^2\) V\(^{-1}\) s\(^{-1}\) under no illumination, extracted in the linear region of the transfer curve and at \(V_{ds} = 1\) V. Upon successive laser irradiations, we observe a photogating effect, whereby the threshold voltage of the transistor shifts to negative gate biases by more than 10 V due to increased electron doping. This has previously been observed in ultrathin TMD FETs and is
attributed to the interaction of photo-generated carriers with charge traps in the transistor channel. At the highest incident power, the FET channel is effectively still open at \( V_g = 60 \) V, where the output current stays firmly above \( 10^{-7} \) A and leads to a large reduction in the ON/OFF ratio of our device.

Figure 2(b) presents the gate curves after plasma treatment. The observed level of output current in the dark transfer curve drops two-fold when evaluated at the gate bias, \( V_g = 60 \) V. Meanwhile, the threshold voltage is seen to shift to more positive gate biases by \( \sim 5 \) V. This shift indicates oxygen-related p-type doping in the material, consistent with previous works on oxygen plasma-treated MoS\(_2\). In addition, the MoS\(_2\) now possesses a weak ambipolar response, indicating hole-branch conduction caused by the likely presence of plasma-created oxides. After 2 s of plasma treatment, the output current in the saturation region of the gate curve improves by one order of magnitude under all illumination powers (note scale on the y-axis). Figure 2(c) tracks the MoS\(_2\) channel field-effect mobility before and after chemical reaction with the plasma. With no laser illumination, the mobility is seen to decrease slightly after 2 s, which we have explored in previous work. After 2 s of exposure, the carrier mobility increases over ten-fold in illuminated gate curves, as the laser power is turned up. We find no clear relationship between the mobility and the laser power for the untreated sample. However, we obtain a good power law fit to the mobility scaling as \( \mu \propto P^{0.13} \) above laser powers of \( 10^{-3} \) mW. The dependence of the photocurrent on the laser power is sublinear, although the power law response is enhanced by plasma treatment from \( \mu \propto P^{0.13} \) to \( \mu \propto P^{0.20} \) (see Fig. S1).

We plot the DC photoresponsivity, \( R_{ph} \), at different gate biases as a function of irradiation power in Fig. 3. \( R_{ph} \) is the current generated in the device per unit of laser power and is a crucial parameter that quantifies the sensitivity of photodetectors. We obtain good linear fits of \( R_{ph} \) as a function of power, \( P \), across the whole gate bias range, before and after plasma treatment. The negative slope in the log-log plot indicates the saturation of trap states in the material with increasing incident optical power. In Fig. 3(a), we see the 0 V and 60 V gate bias trends exhibiting similar levels of \( R_{ph} \), especially at higher laser powers. Upon plasma treatment, in Fig. 3(b), we observe an enhancement of \( R_{ph} \) for all tested gate biases and a notable separation of the responsivity as a function of \( V_g \). As \( V_g \) is increased, the device becomes more responsive to laser illumination. The slope of this relationship depends on the charge trapping rate in the MoS\(_2\) FET channel. Our results suggest that the creation of oxides on the surface inhibits photo-generated pair recombination via defect sites. When compared at \( V_g = 60 \) V where the FET moves into depletion, i.e., the majority carrier concentration in MoS\(_2\) induced by gating begins to approach that of the photogenerated carrier density, the dependence on laser power is stronger for the treated sample. This also serves as a measure of the photogating effect seen in the power-graded transfer curves in Figs. 2(a) and 2(b). An increased response after plasma treatment is thus a direct consequence of the additional charge present in the device, as demonstrated by higher current levels in the gate curves.

The temporal response of the device pre- and post-plasma treatment is charted in Fig. 3(c). The photocurrent is seen to improve two-fold for the tested device when the laser irradiation is modulated through 5 s on/off cycles at a power of 36 mW and \( V_g = 5 \) V. The post-sensitization fall (\( \tau_{fall} \)) and rise (\( \tau_{rise} \)) times are extracted from single exponential fits in Figs. 3(d) and 3(e), respectively. The time-resolved photoresponses compare favorably with the evaporated MoO\(_x\) overlayer report, where our rise time at a much lower irradiation power is 35% shorter. However, the response time of the photo-FET has been sacrificed to achieve favourable responsivity. This is a well-known issue in sensitized MoS\(_2\) photo-FETs arising from carrier trapping, and needs to be addressed in future research on these devices.

Spectroscopic mapping of the samples allows for a closer inspection of the chemical state of the MoS\(_2\) surface pre- and post-plasma treatment. Figures 4(a) and 4(b) show the spatially resolved Raman maps of the material corresponding to the in-plane vibrational mode at 385 cm\(^{-1}\). We notice a drastic drop in the intensity of the signal at this frequency, indicating a change in the MoS\(_2\) lattice which alters the Raman-active modes in the sample. The flake-averaged spectra are presented in Fig. 4(c), demonstrating the quenching effect of plasma treatment on the monolayer MoS\(_2\) Raman peaks. From the spectral component fits (see Table S1), the monolayer nature of the sample is confirmed with a wavenumber separation of 20.5 cm\(^{-1}\) between the \( A' \) and \( E' \) peaks. Upon plasma treatment, the intensity of both Raman modes is severely reduced after 2 s of exposure, while the peak position also shifts and the full-width-at-half-maximum (FWHM) increases. Both the downshift of the \( E' \) peak and upshift of the \( A' \) peak are consistent with reports on molybdenum oxide formation on MoS\(_2\), as is the asymmetric broadening of both peaks. PL maps of the neutral A exciton emission (1.84 eV) of the same flake are presented before and after 2 s of plasma treatment in Figs. 4(d) and 4(e).
Oxides of molybdenum are commonly known as high work function materials (6.8 eV) with a bandgap of 3 eV,12,42 and hence appear darker in secondary electron micrographs than the lower work function MoS2 at this electron beam energy (15 keV). Uniformly distributed plasma-generated oxides spanning tens of nanometers form an effective medium with the unreacted MoS2 in the FET channel, as observed more clearly in the contrast-adjusted inset on the micrograph in Fig. 5(a) (see also scanning transmission electron microscopy results for nanometer-resolved images of pits in our previous work14). As the Fermi level of the donor MoS2 is higher than that of MoOx, significant band bending will occur at the equilibrated interface of the heterojunction.15 Photo-generated holes in MoS2 will become trapped at the junction interface,16 inhibiting radiative recombination and thereby enhancing the photocurrent with electrons as majority carriers, as previously pointed out by Yoo et al.17 and outlined in the band diagram in Fig. 5(b). This observation is also supported by the suppressed radiative recombination observed in the PL data and the strong photogating effect mediated by the electron-rich FET channel. The improved responsivity at higher back-gate fields is a direct consequence of Fermi level alignment which also facilitates easier photocarrier injection into the contacts18,46,47 and primes the device for photon detection levels exceeding those of the pristine MoS2.

In conclusion, we have demonstrated that the photoresponsivity of MoS2 monolayer FETs can be enhanced ten-fold by the introduction of surface-bound molybdenum oxides. The effect of the mobility and photoresponsivity enhancement depends on laser power and is more prominent at powers exceeding several μWatts.

See supplementary material for details on the spectroscopic fits, power dependence of current, 4 s exposure data, and TEM images.

REFERENCES