

# Engineering Chemically Active Defects in Monolayer MoS<sub>2</sub> Transistors via Ion-Beam Irradiation and Their Healing via Vapor Deposition of Alkanethiols

Simone Bertolazzi, Sara Bonacchi, Guangjun Nan, Anton Pershin, David Beljonne, and Paolo Samorì\*

Irradiation of 2D sheets of transition metal dichalcogenides with ion beams has emerged as an effective approach to engineer chemically active defects in 2D materials. In this context, argon-ion bombardment has been utilized to introduce sulfur vacancies in monolayer molybdenum disulfide (MoS<sub>2</sub>). However, a detailed understanding of the effects of generated defects on the functional properties of 2D MoS<sub>2</sub> is still lacking. In this work, the correlation between critical electronic device parameters and the density of sulfur vacancies is systematically investigated through the fabrication and characterization of back-gated monolayer MoS<sub>2</sub> field-effect transistors (FETs) exposed to a variable fluence of low-energy argon ions. The electrical properties of pristine and ion-irradiated FETs can be largely improved/recovered by exposing the devices to vapors of short linear thiolated molecules. Such a solvent-free chemical treatment—carried out strictly under inert atmosphere—rules out secondary healing effects induced by oxygen or oxygen-containing molecules. The results provide a guideline to design monolayer MoS<sub>2</sub> optoelectronic devices with a controlled density of sulfur vacancies, which can be further exploited to introduce ad hoc molecular functionalities by means of thiol chemistry approaches.

Atomically thin semiconductors from the family of transition metal dichalcogenides (TMDCs), such as monolayers of MoS<sub>2</sub>, WS<sub>2</sub>, MoSe<sub>2</sub>, and WSe<sub>2</sub> have been the subject of intense research efforts over the last five years, owing to their sizable direct bandgap (1–3 eV), high charge-carrier mobility (up to  $\approx 100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) and excellent mechanical flexibility that make them attractive components for application in the next-generation flexible (opto)electronics.<sup>[1]</sup> Among these newly emerging 2D semiconductors, monolayer MoS<sub>2</sub> is the prototypical and most investigated to date,<sup>[2]</sup> being the first to be used as active layer in electronic switches<sup>[3]</sup> and optoelectronic

devices, such as photodetectors and solar cells.<sup>[4]</sup> Moreover, recent advances in the large-area growth of 2D MoS<sub>2</sub> crystals by chemical vapor deposition (CVD) have enabled a large number of studies focused on this promising material.<sup>[5]</sup> However, before such impressive pace, research on MoS<sub>2</sub> has been carried out for more than 50 years,<sup>[6]</sup> with relevant experiments conducted in the area of lubrication<sup>[7]</sup> and catalysis.<sup>[8]</sup> The catalytic properties of monolayer MoS<sub>2</sub> have also been the subject of renovated attention. It was recently demonstrated that the inert MoS<sub>2</sub> basal plane could be successfully activated and optimized through the introduction of chemically active defects (i.e., sulfur vacancies) together with strain, resulting in greatly enhanced catalytic activity for hydrogen evolution reaction.<sup>[9]</sup> Sulfur vacancies are known to be present in both CVD-grown and mechanically exfoliated MoS<sub>2</sub> sheets,<sup>[10]</sup> but their density has to be increased and systematically

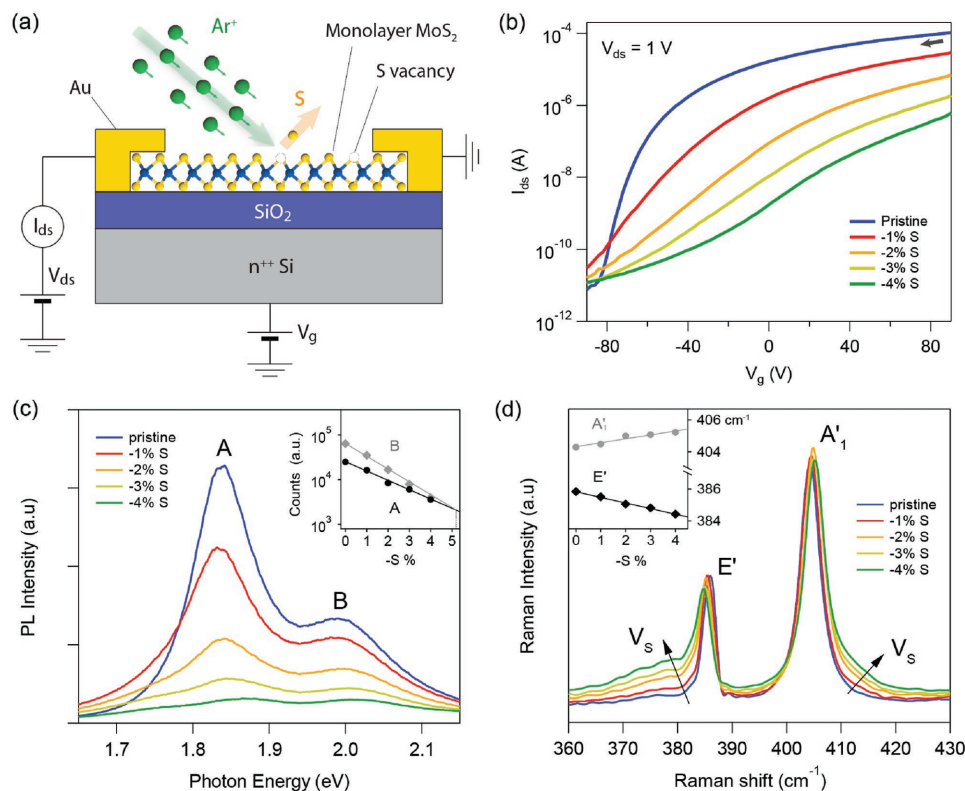
controlled to promote/tune the catalytic activity of the 2D materials. Various approaches have been reported in the literature for modulating the density of sulfur vacancies, namely electron irradiation,<sup>[11]</sup> thermal annealing,<sup>[12]</sup> plasma treatments,<sup>[9,13]</sup> as well as bombardment with charged particles.<sup>[14]</sup> The development of such methods is highly desirable also in the context of chemical functionalization of 2D MoS<sub>2</sub>,<sup>[15]</sup> which is currently under intense investigation for tailoring the material properties, such as electronic doping and optical emission/adsorption to fit the specific requirements of the different applications envisioned for this 2D semiconductor.<sup>[16]</sup> In this framework, various groups have reported that sulfur vacancies, intrinsic or created with a suitable technique, act as anchoring sites for the covalent attachment of small molecules to the surface of MoS<sub>2</sub> via thiol functional groups, enabling a remarkable tuning of its electronic, optical, and vibrational properties.<sup>[12b,17]</sup> Under this perspective, both the implementation of a sound method to control the density of sulfur vacancies and a thorough characterization of their effects on the properties of the 2D sheet are mandatory. In particular, in view of possible applications of chemically functionalized monolayer MoS<sub>2</sub> in electronic devices, such as chemical (bio)sensors,<sup>[18]</sup> it is of great interest to establish a correlation between the density of sulfur vacancies and the

Dr. S. Bertolazzi, Dr. S. Bonacchi, Prof. P. Samorì  
University of Strasbourg  
CNRS, ISIS UMR 7006  
8 allée Gaspard Monge, F-67000 Strasbourg, France  
E-mail: samori@unistra.fr

Dr. G. Nan, Dr. A. Pershin, Dr. D. Beljonne  
Laboratory for Chemistry of Novel Materials  
Université de Mons  
Place du Parc 20, 7000 Mons, Belgium



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**Figure 1.** Effects of Ar-ion irradiation on the properties of 2D MoS<sub>2</sub>. a) Schematic illustration of the ion-bombardment experiment. b) Drain–source current ( $I_{ds}$ ) versus gate voltage ( $V_g$ ) transfer characteristics of a monolayer MoS<sub>2</sub> FET exposed to an increasing fluence of Ar ions. The black arrow indicates the sweep direction, which was the same for all measurements. The density of generated vacancies  $V_S$ , which is expressed as percentage of decrease in the sulfur content (e.g., –1%), has been determined by XPS measurements (Section S1, Supporting Information). c) PL spectra of a mechanically exfoliated monolayer MoS<sub>2</sub> flake on SiO<sub>2</sub>/Si for different  $V_S$  values. The inset (log–lin scale) shows the exponential decrease of the A and B exciton peak intensity with increasing  $V_S$ . d) Raman spectra for the same flake as in (c) showing the main Raman-active phonon modes of MoS<sub>2</sub>, as well as the development of disorder-activated side bands. The  $A'_1$  mode blue shifts, whereas the  $E'$  mode red shifts (inset).

electronic properties of the 2D material. To the best of our knowledge, there are no reports in the literature concerning the measurement of critical field-effect device parameters (e.g., charge-carrier mobility) as a function of sulfur-vacancy density ( $V_S$ ). In this work, we focus our attention on the use of low-energy Ar-ion bombardment<sup>[14b]</sup> to controllably introduce sulfur vacancies in monolayer MoS<sub>2</sub> sheets serving as channel material in back-gated field-effect transistors (FETs). With this approach, we can systematically explore the changes in the electrical characteristics of our FETs with the increasing number of ions impinging on the channel surface, corresponding to a well-defined amount of newly generated sulfur vacancies. We show that the electron field-effect mobility  $\mu_{FE}$  decreases as  $\approx 1/V_S^2$  with increasing density of vacancies up to  $V_S \approx 5\%$ , in line with predictions from a Coulomb impurity (CI) scattering model. Moreover, for  $V_S \geq 20\%$  our transistors display ambipolar behavior, which is consistent with the reduction of energy bandgap predicted by density functional theory (DFT) electronic structure calculations. We also demonstrate that the electrical properties can be largely recovered by exposing the ion-irradiated devices to vapors of short linear molecules with thiol headgroups, such as butanethiols, confirming previous results on defect healing via chemisorption of thiol-terminated molecules at sulfur vacancies.<sup>[17,19]</sup> However, the use of vapors

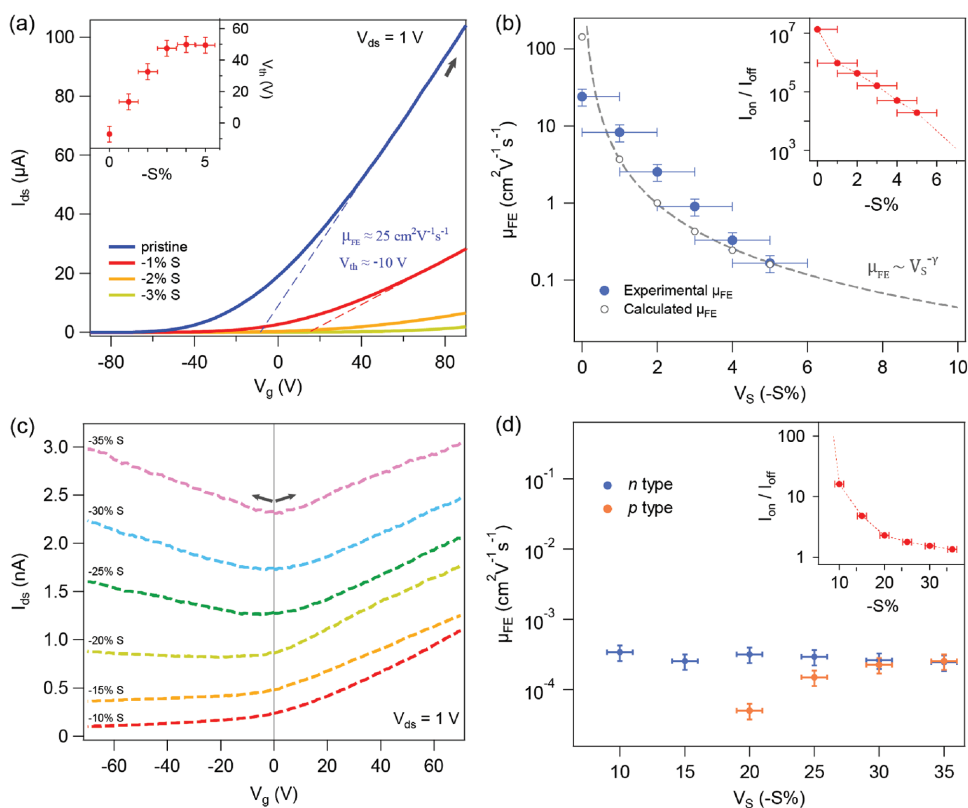
rather than the common solution processing with ethanol was found to be critical to evaluate the efficacy of the thiol chemistry treatment. Besides the charge transport study, this work is complemented with a systematic characterization of ion-irradiated and thiol-treated monolayer MoS<sub>2</sub> sheets by means of Raman and photoluminescence (PL) spectroscopy, which further supports the conclusions.

**Figure 1a** shows the schematics of the ion bombardment experiment, where the channel of a back-gated monolayer MoS<sub>2</sub> FET is exposed to a beam of Ar<sup>+</sup> ions. The bombardment is carried out under high vacuum ( $\approx 10^{-8}$  mbar) by means of a Thermo Fischer EX06 ion gun with acceleration voltage set at 500 V (see the Experimental Section). Previous X-ray photoemission spectroscopy (XPS) studies<sup>[14b]</sup> demonstrated that bombarding monolayer MoS<sub>2</sub> films with Ar<sup>+</sup> ions with kinetic energy of  $\approx 500$  eV allows selective removal of sulfur atoms without affecting the concentration of molybdenum atoms. We performed similar in situ XPS experiments (Section S1, Supporting Information) to evaluate the density of sulfur vacancies  $V_S$  generated by our ion-bombardment procedure. For an ion fluence  $F \approx 8.2 \times 10^{12}$  ions  $\cdot$  cm<sup>-2</sup>, the density of generated sulfur vacancies was found to be  $V_S \approx 2.3 \times 10^{13}$  cm<sup>-2</sup>, which corresponds to a relative change in the sulfur content  $\Delta S/S \approx -1\%$ . We point out here that  $V_S$  is intended as the density of sulfur vacancies induced by

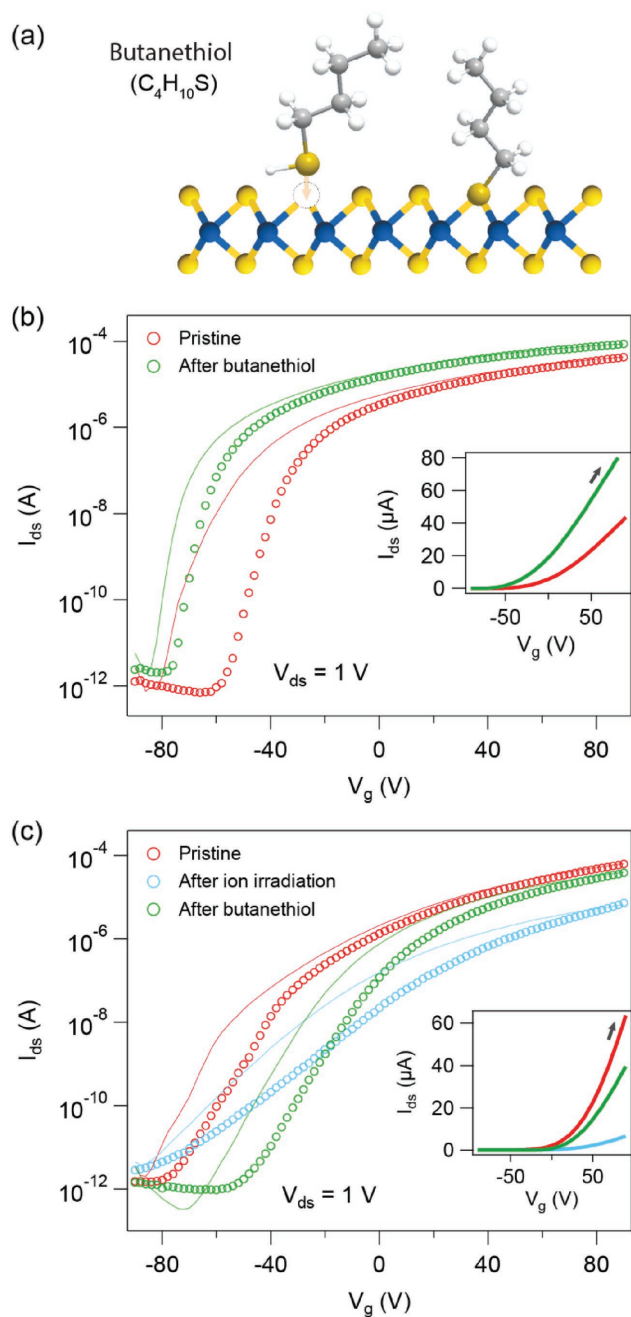
the bombardment process and it is assumed for simplicity that the amount of vacancies in the pristine (not bombarded) material is comparatively negligible. After obtaining the relationship between  $F$  and  $V_S$  (Figure S2, Supporting Information), we proceeded to bombard our monolayer MoS<sub>2</sub> FETs with a variable fluence of Ar<sup>+</sup> ions. The experiment was carried out in multiple bombardment steps; at each step the devices were irradiated with an incremental fluence  $\Delta F \approx 8.2 \times 10^{12}$  ions·cm<sup>-2</sup>—in order to reduce the relative sulfur content by  $\approx 1\%$ —and were subsequently taken out from the vacuum chamber and electrically characterized under N<sub>2</sub> atmosphere. The devices were not exposed to ambient air between ion bombardment and electrical measurements (see the Experimental Section). Figure 1b displays a typical set of transfer curves (drain–source current  $I_{ds}$  vs gate voltage  $V_g$ ) measured on the same monolayer MoS<sub>2</sub> FET at different steps of the ion-bombardment process. It can be seen that the ON-current level decreases monotonically with  $V_S$  and the switching capability of the transistor becomes gradually compromised. Figure 1c compares the PL spectra of a mechanically exfoliated monolayer MoS<sub>2</sub> flake acquired for different values of ion fluence (equivalently  $V_S$ ). The panel inset displays the intensities of the A and B exciton peaks as a function of  $V_S$ , which decrease exponentially and cross each other at  $V_S \approx 5.2\%$  (corresponding to a fluence  $F \approx 4.3 \times 10^{13}$  ions·cm<sup>-2</sup>).

Furthermore, we noticed the occurrence of a slight blue shift for both A and B exciton peaks, as well as the development of a sub-bandgap PL emission peak at  $E_d \approx 1.75$  eV (Figure S10, Supporting Information). Defect-induced PL emission in semiconducting TMDCs has been previously investigated,<sup>[14a]</sup> revealing the emergence of a new peak (1.78 eV) in the PL spectra of monolayer MoS<sub>2</sub> sheets irradiated with  $\alpha$  particles or thermally annealed at  $\approx 500$  °C in order to create sulfur vacancies; the peak was attributed to the radiative recombination of neutral excitons bound to defect states. The evolution of the two main Raman-active phonon modes, namely the polar  $E'$  and the homopolar  $A'_1$  optical phonon modes, is presented in Figure 1d. The most remarkable features are the blue (red) shift of the  $A'_1$  ( $E'$ ) mode, displayed in the panel inset, as well as the development of two disorder-activated Raman bands<sup>[20]</sup> at frequencies higher and lower than the  $A'_1$  and  $E'$  peaks, respectively.

The devices fabricated in this work exhibited a two-terminal electron field-effect mobility  $\mu_{FE}$  within the range 10–30 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, whereas the mobility extracted using the four-terminal measurement configuration ranged between 20 and 40 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, approaching the values obtained with unencapsulated FETs on SiO<sub>2</sub>/Si substrates in high-vacuum conditions.<sup>[21]</sup> The measurements were in fact carried out using both two-probe and four-probe configurations (see Section S2.1



**Figure 2.** Impact of sulfur vacancies on charge transport. a) Transfer characteristics ( $I_{ds}$  vs  $V_g$ ) of a monolayer MoS<sub>2</sub> FET exposed to an incremental dose of Ar ions (solid lines). The dashed lines correspond to the linear fitting from which  $\mu_{FE}$  and  $V_{th}$  were extracted. Inset: plot of  $V_{th}$  as a function of  $V_S$ . b) Measured (blue circles) and calculated (white circles)  $\mu_{FE}$  for  $V_S$  values up to 5%. The gray dashed line represents the power-law trend with fall-off parameter  $\gamma = 1.93$ . Inset: plot of  $I_{ON}/I_{OFF}$  as a function of  $V_S$ . c) Transfer curves for  $V_S$  values within the range 10%–35%. To avoid slow charging/discharging effects upon application of a gate voltage bias (see Section S2.2 in the Supporting Information), the curves were acquired in two steps as indicated by the arrows, gradually increasing (decreasing) the gate voltage from 0 to 90 V (–90 V). d) Experimental n and p-type field-effect mobility for  $V_S > 5\%$ . Inset:  $I_{ON}/I_{OFF}$  versus  $V_S$  data plot. Device dimensions:  $L = 0.8$   $\mu\text{m}$  and  $W = 2.8$   $\mu\text{m}$ .



**Figure 3.** Charge transport in chemically-treated monolayer MoS<sub>2</sub> FETs. a) Schematic drawing of the healing process: butanethiol molecules fill the sulfur vacancies via covalent interaction with unsaturated molybdenum atoms. b) Transfer characteristics in log–lin scale—acquired with sweep direction from +90 to –90 V—of a pristine monolayer MoS<sub>2</sub> FET before (red circles) and after (green circles) exposure to butanethiol vapors. The solid lines correspond to the opposite sweep direction and are shown also in lin–lin scale in the inset. c) Same curves as in (b) for a device that underwent an intermediate step of ion bombardment (light-blue curves), which generated sulfur vacancies with a density  $V_s \approx 3\%$ .

in the Supporting Information) to confirm that the changes in the electrical characteristics of the ion-irradiated FETs stemmed from the transistor channel itself and not from variations in the contact resistance. **Figure 2a** portrays the two-terminal transfer

characteristics of a typical monolayer MoS<sub>2</sub> FET that underwent the ion-bombardment procedure. After irradiating the device with an ion fluence  $F \approx 8.2 \times 10^{12}$  ions · cm<sup>-2</sup> (i.e.,  $\Delta S/S \approx -1\%$ ) the mobility  $\mu_{FE}$  drops from  $\approx 25$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> to  $\approx 8$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> while the threshold voltage  $V_{th}$  shifts toward positive  $V_g$  values by an amount  $\Delta V_{th} \approx +20.5$  V, which corresponds to a change in the carrier density  $\Delta n_{th} \approx 1.5 \times 10^{12}$  cm<sup>-2</sup>. The positive shift of  $V_{th}$  indicates that newly created defect states have to be filled before reaching the linear regime of the  $I_{ds}$  versus  $V_g$  transfer curves associated with conduction-band transport. Defect states are responsible for reducing the fraction of mobile carriers in the conduction band; at the same time they increase the fraction of trapped carriers that do not contribute to charge transport, resulting in a degraded effective mobility.<sup>[22]</sup> In agreement with previous reports,<sup>[17c]</sup> we found that the sulfur vacancies act as trap states, as it can be inferred by considering that  $\Delta n_{th}$  scales with the amount of vacancies introduced with ion bombardment. In fact, with further increase of  $V_s$ , the threshold voltage  $V_{th}$  was found to shift toward larger positive values, as shown in the panel inset. For  $V_s \geq 3\%$  an unambiguous linear regime could not be identified within the gate-voltage range used in the experiment, which is the reason behind the saturation appearing in the  $V_{th}$  versus  $V_s$  plot (inset, Figure 2a). To elucidate the exact nature of charge transport at various levels of disorder, temperature-dependent studies ought to be performed, which is however beyond the scope of the present work. We rather resorted to modeling. Based on DFT electronic structure calculations of pristine MoS<sub>2</sub> monolayers, we applied the semiclassical Boltzmann transport theory in the relaxation time approximation, including scattering by both phonons and CIs generated by charge filling at sulfur vacancies (see Section S5 in the Supporting Information). The band electron mobility values were corrected to account for the nonlinear dependence of mobile, free, charge carriers with gate voltage, as previously proposed.<sup>[22]</sup> The resulting field-effect mobilities, reported in Figure 2b (white circles), show a power-law dependence with the concentration of sulfur vacancies ( $\mu_{FE} \propto V_s^{-\gamma}$ ) with a fall-off parameter  $\gamma$  close to 2 ( $\gamma = 1.93$ ). Such an evolution arises from the combined effect of CI scattering and the free versus total charge density renormalization factor, both scaling as  $1/V_s$ . Figure 2b displays the experimental mobilities (blue circles) obtained from linear fitting of the two-terminal transfer curves in the high positive gate-voltage range (70–90 V). When using in the charge transport simulations a total electron density of  $1.5 \times 10^{13}$  cm<sup>-2</sup>—in line with Hall-effect measurements<sup>[23]</sup> performed on back-gated FETs with similar oxide thickness and high n-doping level—a satisfactory agreement is found between theory and experiment for  $V_s$  values up to 5%. Instead, beyond 5% the predicted mobilities largely exceed the experimental data, likely suggesting a breakdown of the band model used here and the predominance of hopping transport. For  $V_s \geq 10\%$ , the experimental  $\mu_{FE}$  forms a plateau at  $\approx 2 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and  $I_{ON}/I_{OFF}$  becomes definitively smaller than 10, indicating the almost complete loss of the device switching capability. At the same time, new interesting features can be observed in the transfer characteristics, see Figure 2c. Firstly, with increasing  $V_s$ , the curves undergo a vertical shift in the graph, i.e., the overall conductivity of the 2D MoS<sub>2</sub> sheet increases due to the larger amount of localized defect states

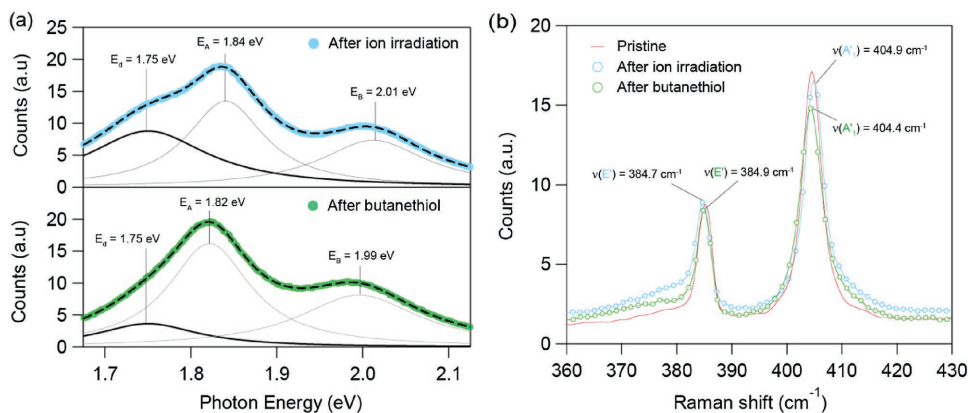


available for hopping-type charge transport. Secondly, for  $V_S \geq 20\%$ , the FETs display ambipolar behavior, where the p-type mobility increases with  $V_S$  and matches the n-type counterpart at  $V_S \approx 35\%$  (Figure 2d). This suggests the occurrence of a rearrangement in the band structure of the 2D semiconductor associated with a reduction of its bandgap, as demonstrated by DFT electronic structure calculations for sulfur vacancy contents ranging from 0 up to 25% (see Section S6 in the Supporting Information).

After elucidating the influence of ion-beam induced sulfur vacancies on the electrical transport properties of monolayer MoS<sub>2</sub>, we explored the efficacy of chemical treatments with thiol molecules. Here we used one among the shortest thiol-terminated linear molecules, namely butanethiol (C<sub>4</sub>H<sub>10</sub>S, Figure 3a). The chain length was minimized in order to promote the edge-on surface-molecule orientation, with the aim of (i) reducing the steric hindrance hampering the filling of neighboring sulfur vacancies and (ii) minimize the electronic coupling of the molecule with the MoS<sub>2</sub> surface, which is expected to act as a source of electronic disorder detrimental for charge transport. In the first attempt, we performed the chemical treatment using previously published methods based on solutions of thiol molecules in ethanol.<sup>[12b,17b]</sup> However, control experiments carried out only in the presence of neat ethanol (anhydrous,  $\leq 0.003\%$  water) unexpectedly revealed a nonnegligible recovery of the electrical characteristics of the ion-irradiated FETs (see Section S2.4 in the Supporting Information). Such finding is nevertheless very reasonable since oxygen and sulfur are valence isoelectronic atoms, and oxygen-containing molecules can also contribute to defect healing via strong chemical interaction with unsaturated molybdenum atoms.<sup>[24]</sup> Moreover, the presence of multiple sulfur vacancies, which are likely to be generated during Ar-ion bombardment,<sup>[25]</sup> could increase significantly the reactivity of the MoS<sub>2</sub> basal plane with such molecular species. Therefore, we implemented a vapor-phase treatment to exclude secondary healing mechanisms (see the Experimental Section). First, we show the effects induced by butanethiol molecules on the transfer characteristics of

pristine FETs (Figure 3b). The treatment with short thiol molecules augments the ON-current level, reduces the hysteresis and increases the field-effect mobility (from  $\approx 21$  to  $\approx 33 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ), which is consistent with the reduction of charge traps associated with sulfur vacancies in the pristine MoS<sub>2</sub> sheets. Conversely, the use of long alkanethiol molecules, such as hexadecanethiol (HS(CH<sub>2</sub>)<sub>15</sub>CH<sub>3</sub>), was reported to reduce both the charge-carrier mobility and the ON current level.<sup>[17b]</sup> Afterward, we tested the efficacy of our method on ion-irradiated devices with a density of generated vacancies  $V_S \approx 3\%$ . Figure 3 shows the effects on the transfer characteristics: after treatment (green circles) a remarkable recovery was obtained from the degraded condition set by ion bombardment (light-blue circles). The butanethiol treatment enhanced the  $I_{\text{ON}}/I_{\text{OFF}}$  ratio from  $\approx 2 \times 10^6$  to  $\approx 4 \times 10^7$  and the field-effect mobility from  $\approx 1.4$  to  $\approx 8.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . Using the power-law trend  $\mu_{\text{FE}} \propto V_S^{-7}$  we could estimate a sulfur-vacancy density post treatment of  $\approx 1.2\%$ , which represents a clear improvement over the pretreatment condition ( $V_S \approx 3\%$ ). PL and Raman spectroscopy measurements display as well signatures of defect healing. Figure 4a compares the PL spectra of an ion-irradiated MoS<sub>2</sub> sheet, before and after exposure to butanethiol vapors. Upon treatment, both A and B exciton peaks red shift (10–20 meV), the defect-mediated emission peak at  $E_d \approx 1.75 \text{ eV}$  remarkably decreases whereas the A exciton peak increases. At the same time, the Raman spectra (Figure 4b) show a damping of the disorder-activated side bands together with a blue shift and red shift of the  $E'$  and  $A'_1$  peaks, respectively, consistent with the reduction of sulfur vacancies (see Figure 1d for comparison). Finally, control experiments were performed with vapors of an analogous molecule without thiol anchoring group, i.e., pentane (C<sub>5</sub>H<sub>12</sub>, see Figure S9 in the Supporting Information), which were not found to improve/recover the devices' electrical properties.

In summary, we demonstrated that low-energy Ar-ion irradiation can be effectively employed to create sulfur vacancies in 2D sheets of MoS<sub>2</sub> enabling a systematic control over defect density. Ion beams can be rastered over centimeter-scale large



**Figure 4.** Effects of butanethiol on PL and Raman spectra. a) PL spectra of a monolayer MoS<sub>2</sub> flake acquired after ion irradiation ( $V_S \approx 3\%$ , top) and after treatment with butanethiol (bottom). The spectra were fitted with a triple Lorentzian function (dashed lines) to take into account the defect-mediated emission occurring at  $E_d \approx 1.75 \text{ eV}$ . The individual Lorentzian components are shown in solid lines. For simplicity, the A exciton/trion peak was taken as one. b) Raman spectra of the same flake as in (a) acquired after ion irradiation (light blue) and after exposure to butanethiol vapors (green). For comparison, the spectrum of the pristine flake is also shown (red line). PL and Raman peak positions were rounded to the nearest hundredth and tenth, respectively.

areas in relatively short times—as compared to their electron counterpart—and could be further adapted for direct patterning of defective regions in CVD-grown films of MoS<sub>2</sub>, which would not be feasible with thermal annealing or plasma treatments that act on the entire sample surface. For the first time to our knowledge, the effects of ion-beam generated sulfur vacancies on the electrical characteristics of monolayer MoS<sub>2</sub> FETs were elucidated by establishing a correlation between critical device parameters and the density of generated sulfur vacancies. Moreover, we employed a new chemical treatment based on vapors of short thiol-terminated molecules that allowed improving the electrical properties of pristine FETs and enabled a significant recovery of the performance of ion-irradiated FETs. Our solvent-free procedure—carried out strictly under inert atmosphere—rules out secondary healing effects by oxygen or oxygen-containing molecules, such as ethanol, and could be further exploited to functionalize 2D MoS<sub>2</sub> sheets with a virtually infinite number of molecules possessing thiol functional groups. Our findings represent a guideline for the trade-off choice between electronic device performance and density of chemically active defects suitable for chemical functionalization.

## Experimental Section

**Ion Bombardment:** Ar-ion bombardment of monolayer MoS<sub>2</sub> FETs was performed by means of a Thermo Fischer EX06 ion gun with acceleration voltage of 500 V. The angle between the ion beam and the substrate surface normal was ≈58°. To avoid shadow effects due to the metal contact thickness, the FETs were oriented with their channel-width direction parallel to the projection of the ion beam on the sample surface. The ion-beam ( $I \approx 210$  nA) was uniformly raster-scanned over a rectangular area of ≈8 × 4 mm<sup>2</sup> (see Section S1 in the Supporting Information).

**Device Fabrication and Electrical Characterization:** Monolayer MoS<sub>2</sub> flakes were mechanically exfoliated from commercially available molybdenite crystals (Furuchi, Japan) and were identified through a combination of optical microscopy, Raman, and PL spectroscopy. Back-gated FETs with two-probe and four-probe geometry were fabricated on thermally oxidized heavily n-doped silicon substrates ( $\rho_{Si} \approx 0.001$  Ω-cm,  $t_{ox} = 290$  nm) by means of e-beam lithography with a double-layer of polymethyl methacrylate, thermal evaporation of Au (85 nm) and lift-off in warm acetone (≈50 °C). As-fabricated devices were annealed at 140 °C for ≈15 h inside a high-vacuum chamber (≈5 × 10<sup>-8</sup> mbar) to reduce contact resistance and desorb atmospheric adsorbates.<sup>[26]</sup> Importantly, the FETs were no longer exposed to air after annealing and were electrically characterized only under inert atmosphere (N<sub>2</sub>-filled glovebox). Electrical measurements were carried out at room temperature with source-measurement units from Keithley (model 2636A).

**Raman and Photoluminescence Spectroscopy:** Raman and PL spectra were acquired at room temperature with a Renishaw InVia spectrometer equipped with a 532 nm laser. The measurements were carried out in air using a 100× lens objective (numerical aperture NA = 0.85) providing a beam spot size of ≈700 nm. The excitation power was kept below 1 mW to avoid local heating damage effects. For Raman (PL) measurements, the wavenumber (energy) resolution was ≈1.25 cm<sup>-1</sup> (≈1 meV). The continuous-lines Raman spectra are obtained with the cardinal spline interpolation method. The Si band at 520.3 cm<sup>-1</sup> was used for normalization.

**Chemical Treatment with Butanethiol Vapors:** The substrates holding the FETs were fixed onto the lid of a 20 mL glass container filled with 200 μL of 1-butanethiol (99%, Sigma Aldrich). The lid was closed, with the sample surface facing the liquid, and the container was saturated

with butanethiol vapor by heating for 3 h at 70 °C. The samples were then placed on a hot plate and annealed for 1 h at 70 °C to remove non-chemisorbed molecules. All the process was carried out under inert atmosphere (N<sub>2</sub>-filled glovebox).

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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