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Gas dependent hysteresis in MoS2 field effect transistors

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Abstract

We study the effect of electric stress, gas pressure and gas type on the hysteresis in the transfer characteristics of monolayer molybdenum disulfide (MoS2) field effect transistors. The presence of defects and point vacancies in the MoS2 crystal structure facilitates the adsorption of oxygen, nitrogen, hydrogen or methane, which strongly affect the transistor electrical characteristics. Although the gas adsorption does not modify the conduction type, we demonstrate a correlation between hysteresis width and adsorption energy onto the MoS2 surface. We show that hysteresis is controllable by pressure and/or gas type. Hysteresis features two well-separated current levels, especially when gases are stably adsorbed on the channel, which can be exploited in memory devices.

Introduction

During the last few years, there has been an increasing interest in two-dimensional (2D) materials for technological applications. The presence of a tunable and layer-sizable bandgap, the mechanical strength and the chemical and thermal stability make 2D transition metal dichalcogenides (TMDs) good candidates for next-generation electronic devices [1–6]. Theoretical and experimental studies have demonstrated that 2D TMDs based devices can achieve carrier mobilities up to hundreds cm² V⁻¹ s⁻¹, very high on/off ratios up to 10⁶, low power consumption and short switching times [7–14]. In their 2D form, owing to the low density of states, TMDs enable enhanced gate control in easy-to-fabricate transistors immune from short-channel effects. Indeed, compared to silicon traditional devices, TMD field-effect transistors (FET) show steeper subthreshold swing (SS), negligible drain-induced barrier lowering (DIBL), high drive current capabilities and low standby off-current, even when relatively thick gate oxides are used [15, 16]. The control of n- or p-type conduction is another important advantage offered by TMDs transistors. Indeed, ambipolar conduction and high on/off ratio are important features for stable low-power consumption and performant logic applications [17, 18]. Furthermore, TMDs can be integrated into silicon fabrication technologies to realize devices with nanometric channel length, suitable for high-density integrated circuits.

Additional features like photoconductivity [6, 19] and spin-orbit splitting [20] have been investigated for optoelectronic and spintronic applications [21]. Moreover, the sharp edges of TMD flakes, combined with intrinsic doping and low electron affinities, make TMDs promising materials also for field emission devices for vacuum electronics applications [22–29].

Owing to the high surface-to-volume ratio, TMDs have excellent sensing performances. The MoS2 sensitivity to NO and NO2 has been demonstrated [30] with a detection limit of 0.8 ppm, but the exposure to other gases (studied from the theoretical point of view [31, 32]) remains experimentally unexplored.

A considerable number of studies have been also devoted to the effects of the environment on mono- and few-layer TMD devices [33, 34]. For instance, it has been shown that WSe2 is very sensitive to pressure which can tune the conduction type [33]. Similarly, PdSe2, which is a relatively new 2D material, has been demonstrated to be a good gas and pressure sensor [34].
A major difficulty that TMD-based nanoelectronics has to overcome is related to point defects as well as structural damages and dislocations, often generated during the fabrication, independently of the used process such as chemical vapor deposition (CVD) or mechanical exfoliation. Structural defects behave as charge traps and scattering centers, which modify the electronic properties of the devices and generate unwanted hysteresis and/or reduction of conductivity [3, 35, 36]. Hysteresis consists of a shift of the transistor transfer characteristic for consecutive forward/reverse gate voltage sweeps and changes the threshold voltage; it is an unwanted effect to circuits’ designers, as it makes the transistor dependent on the biasing history. In spite of that, hysteresis can be conveniently exploited for the fabrication of memory devices [37–39], since it features two distinct and stable states, that can be used to define the bits of a memory cell. In this regard, it is interesting and important to understand the physical properties that control the hysteretic behavior of the transfer characteristic in TMD transistors.

In this paper, the electric properties of CVD-grown monolayer MoS2 field effect transistors are studied under external stimuli, such as gate voltage, sweep delay time, pressure and pure gas environment, with particular attention to hysteresis. MoS2 was selected among other TMDs because of its layer dependent bandgap over a wide range (1.2–1.9 eV), stability in air and mobility of few tens cm2 V−1 s−1 when deposited on SiO2 [4, 7, 8, 40].

Chalcogen vacancies favor a natural n-type doping in MoS2 and act as trap centers that enhance the hysteretic behavior in MoS2 and others 2D TMDs [19, 34, 41]. We demonstrate exponential dependence of the hysteresis on the sweeping time and a linear dependence on the gate voltage range. We also show that exposure to gases such as oxygen, nitrogen and hydrogen at different pressure modifies the electrical properties of the devices [42], a feature that can be exploited for gas sensing purposes. In addition we prove that defective MoS2 flakes are strongly sensitive to gases like methane (CH4), as anticipated by DFT (density functional theory) studies [43]. We finally show that the wide hysteresis, especially if enhanced by gas adsorption, enables a two-bit memory device featuring a charge retention on the time scale of several minutes and an endurance on the order of hundreds of cycles.

Methods

The MoS2 flakes were grown in a three-zone split tube furnace (ThermConcept), purged with 500 N cm−2 of Ar gas for 15 min to minimize the O2 content. The growing Si/SiO2 substrate was spin coated with a 1% sodium cholate solution, then a saturated ammonium heptamolybdate (AHM) solution served as the molybdenum feedstock. The target material was placed in one zone of the three-zone tube furnace along with 50 mg of S powder, positioned upstream in a separate heating zone. The zone containing the S and AHM were heated to 150 °C and 750 °C, respectively. After 15 min of growth, the process was stopped, and the sample was cooled rapidly.

Raman and atomic force microscopy (AFM) measurements were used to identify monolayer MoS2 among the randomly distributed CVD-grown flakes. Using the substrate as common back-gate, we realized back-gated transistors by evaporating the drain and source electrodes on selected single layer flakes (see figure 1) by means of standard photolithography and liftoff process.

The contacts were made of Ti (10 nm) and Au (100 nm), deposited as adhesion and cover layers, respectively.

In the following, the electrical characterization refers to the inner contacts 1 and 2 as displayed in figure 1(a). Measurements were carried out inside a scanning electron microscope chamber (SEM, LEO 1530, Zeiss), equipped with two metallic tips, with curvature radius of about 100 nm (figure 1(b)) and nanometric positioning capability, connected to a Keithley 4200 SCS (source measurement units, Tektronix Inc.), at room temperature and different chamber pressures, from ~ 10−6 Torr to 760 Torr.

The selected flake was characterized by AFM and Raman/photoluminescence (PL) measurements (Renishaw InVia Raman spectrometer with 532 nm laser wavelength). The results shown in figures 1(c) and (d) prove that the flake is a single layer, as both the step height of ~ 0.75 nm and the large PL peak at ~ 1.85 eV, correspond to the typical height and bandgap values for a monolayer. We note that PL intensity and the AFM step height point to absence of intercalated water at the SiO2/MoS2 interface, owing to high growth temperatures of 750 °C.

Results

The electrical characterization of the device starts with the output and transfer characteristics, as shown in figure 2, measured at 10−6 Torr. To avoid device damage, the channel current and the gate voltage were limited to 1 µA and 50 V, respectively. The output characteristics of figure 2(a) show a slightly rectifying behavior typical of TMD transistors, where Schottky barriers between the channel and the contacts are easily formed [35–37]. Figure 2(b) confirms a normally-on n-type transistor with on/off ratio of ~6 orders of magnitude, featuring a subthreshold swing SS = d(Vth)/d( log₁₀(IDS)) ~ 1 V/dec.

From the relation between mobility and gate voltage, μ = d( IDS)/d(VGS) W Cox, where Cox is the SiO2 capacitance per unit area (11 nF cm−2 for an oxide thickness of 300 nm), Vth the voltage bias and d( IDS)/d(V GS) the transconductance (obtained as the slope of the transfer characteristic at high Vth), we derived a mobility of ~ 1 cm2 V−1 s−1.
This slightly low mobility, likely worsened also by the contact resistance [44–46], suggests the presence of trap states. Three types of trap states can be distinguished, as illustrated in figure 3(a): The adsorbates on the MoS$_2$ surface (1), the intrinsic defects in the crystal structure of MoS$_2$ (2), and the extrinsic traps at the MoS$_2$/SiO$_2$ interface or into the SiO$_2$ dielectric layer (3). Each trap state is characterized by a trapping/detrapping time constant, which can be evaluated by several techniques.

A long annealing in high vacuum can remove most of the adsorbates (1) and allow the investigation of the effect of traps (2) and (3) only.

The transfer curve measured after 24 h at 25°C and ~10$^{-6}$ Torr shows a clockwise hysteretic behavior when the gate voltage is swept forth and back (figure 3(b)). The right-shift of the transfer after a forward $V_{gs}$ sweep corresponds to negative charge trapping. Hysteresis can be characterized by a hysteresis width, $H_W$, defined as the difference of the gate voltages corresponding to the current of 0.1 nA. The hysteretic behavior is investigated as a function of the gate voltage range and the sweeping time in figures 3(c) and (d). A linear dependence of $H_W$ on the gate voltage range is shown in the inset of figure 3(c), while an exponential growth of $H_W$ with the sweeping time is reported in figure 3(e).
linear increase of $H_W$ with the gate voltage range indicates that the trapped charge is proportional to gate potential, as expected considering that the trapping process loads the capacitor formed by the MoS$_2$ channel and the Si substrate. The exponential growth of $H_W$ with the sweeping time [47] characterized by a long time constant of $\sim 24$ min, indicates a predominant role of slow (deep) traps either in MoS$_2$ or in the SiO$_2$ insulator (see (2) and (3) in figure 3(a)).

More insight can be gained observing the transient behavior of the device under a gate voltage pulse. Figure 3(f) shows the channel current during a gate pulse of height 50 V and width $\sim 400$ s. The best fit is provided by a double exponential decay, $I_{ds} = a \exp\left(-\frac{t}{\tau_1}\right) + b \exp\left(-\frac{t}{\tau_2}\right)$, characterized by decay constants $\tau_1 \sim 20$ s and $\tau_2 \sim 1350$ s (i.e. $\sim 23$ min), respectively. Such a behavior points to the presence of two types of electron trap states. The faster trapping is related to MoS$_2$ defects or MoS$_2$/SiO$_2$ interface trap states [48–50], while the slower trapping is ascribed to the filling of trap states inside the SiO$_2$ dielectric, controlled by the gate circuit. The exponential behavior of $H_W$ with the sweeping time indicates that the slower component is dominant when slow gate sweeps are applied. Following the procedure proposed by Xu et al [35], we estimated a density of trap state in the MoS$_2$ structure of $\sim 10^{12} \text{ cm}^{-2} \text{ eV}^{-1}$ in agreement with other values reported in literature [51], using the transfer of figure 3(b), corresponding to the fastest sweep (4 min).

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metrics to check its effect we chose the on-current and the channel mobility, as shown in figure 4(b).

A monotonic change of the conduction parameters occurs while raising the pressure from $10^{-6}$ to 760 Torr. When the chamber is brought to atmospheric pressure in O$_2$ environment, a reduction of the on-current of one order of magnitude and an 80% decrease of the mobility are observed, owing to the adsorption of oxygen. Being highly electronegative, oxygen has an acceptor nature and traps electrons. This reduces the FET current and increases the coulomb scattering that degrades the channel mobility [36]. The compressive stress, applied by pressure to the MoS$_2$ channel, favors the interaction with the supporting SiO$_2$ dielectric and acts as a further mobility suppressor. The increased interaction with the substrate also facilitates charge transfer and contributes to hysteresis (see inset of figure 4(a)).

Figure 4(c) shows the transfer characteristics measured in vacuum ($\sim 10^{-6}$ Torr, solid pink curve) and in 760 Torr atmospheres of pure Ar, H$_2$, O$_2$, N$_2$ and CH$_4$, respectively. Such gases were chosen because of their great interest for gas detection and storage applications and for the availability of theoretical results based on DFT calculations.

The hysteresis can be related to the adsorption energy ($E_{ads}$) of the various gases, defined as the difference

![Figure 4](image-url)

**Figure 4.** (a) Transfer characteristics at different O$_2$ pressures. (b) On-current (at $V_g = 30$ V and $V_d = -1$ V) and field effect mobility versus gas pressure. (c) Transfer characteristics measured under different gas atmospheres (Ar, H$_2$, O$_2$, N$_2$ and CH$_4$) at 760 Torr and in vacuum ($\sim 10^{-6}$ Torr). (d) Hysteresis width versus gas adsorption energy on MoS$_2$ ($E_{ads}$) for H$_2$ and O$_2$ from [31], N$_2$ from [54], CH$_4$ from [43]), as obtained from the sets of $I_d - V_g$ curves corresponding to $-30 \leq V_g \leq 30$ V (figure (c)). Given the linear relation between hysteresis width and gate voltage range (displayed in figure 3(c)), we note that the $H_W - |E_{ads}|$ trend does not change for different gate voltage range choices. For display purposes, the adsorption energy corresponding to Ar and vacuum are set to 1 meV (no estimation of the $E_{ads}$ is currently available for Ar–MoS$_2$ system, while it results in the range 1–10 meV for Ar-carbon allotrope systems [56]). (e) Transfer characteristics and (f) hysteresis width when the pressure is raised from $10^{-6}$ Torr to 760 Torr and then decreased to $10^{-6}$ Torr, in H$_2$ environment.
between the total energy of the system (\(E_{\text{MoS}_2+\text{gas}}\)) and that of MoS\(_2\) and the gas phase molecules alone (\(E_{\text{MoS}_2}\) and \(E_{\text{gas}}\) respectively)

\[E_{\text{ads}} = E_{\text{MoS}_2+\text{gas}} - E_{\text{MoS}_2} - E_{\text{gas}}.\]

The adsorption energies were calculated through computational methods (DFT and \textit{ab initio} studies), and the more negative is the adsorption energy the stronger is the interaction with MoS\(_2\), that is the stability of the MoS\(_2+\)gas system \([31, 42, 43, 52–55]\).

The hysteresis width, evaluated at \(10^{-11}\) A in figure 4(c), as a function of the adsorption energy is displayed in figure 4(d).

The adsorption of Ar on MoS\(_2\) has not been clearly investigated to date; for display purpose, we assumed \(E_{\text{ads}} = 1\) meV in figure 4(d). Ar could contribute to hysteresis, the width of which shows an increase of about 15 V with respect to vacuum, either by adsorption or by increasing the adhesion of the MoS\(_2\) flake on the substrate, as pure pressure effect at 760 Torr \([52]\), which increments the role of the interfacial and SiO\(_2\) traps.

The comparison between transfer characteristics in different gas atmospheres (figure 4(c)) reveals that oxygen, nitrogen, hydrogen and methane strongly affect the MoS\(_2\) electrical features, with a monotonic trend of \(H_W\). This feature points to the suitability of MoS\(_2\) FETs for gas sensing. Such an application is also corroborated by the observation that the effect of gases is reversible. Indeed, figures 4(e) and (f) show that the transfer characteristic modified by the injection of a gas (H\(_2\) in the example) returns about to the initial state when vacuum is restored.

The effect of H\(_2\) on MoS\(_2\) nanostructures has been reported in connection with hydrogen storage application \([42]\), while the effect of CH\(_4\) has been anticipated by DFT studies dealing with low-defective few-layer MoS\(_2\) crystals \([43, 54]\). Indeed, the adsorption of CH\(_4\) on the MoS\(_2\) channel of the device under study confirms the presence of defects, since DFT study indicate positive adsorption energy (i.e. repulsion) of CH\(_4\) on perfect monolayer MoS\(_2\) \([43]\). Defects play an important role in the \(H_W - |E_{\text{ads}}|\) relationship, as gas molecules are mainly adsorbed at the lattice defect sites, because of dangling bonds. The higher is the adsorption energy, the stronger is the interaction of the adsorbed molecules with MoS\(_2\) lattice, which favors the charge exchange that is cause of hysteresis. Furthermore, dissociated and non-dissociated molecules act differently on MoS\(_2\) electronic structure. Non-dissociated molecules, like H\(_2\) and N\(_2\), adsorbed on the MoS\(_2\) surface, define additional trap centers without changing the band-structure. Conversely, dissociated molecules like O\(_2\) modify the MoS\(_2\) band structure by adding inter-band states \([57]\). Moreover, the adsorption of CH\(_4\) on MoS\(_2\) surface generates a d-MoS\(_2/p\)-CH\(_4\) orbital coupling, inducing a net transfer of charge \([43]\).

Finally, we show that the hysteresis in transfer characteristic can be exploited to realize a memory device. Figure 5 reports measurements for single and multiple set-read-reset-read cycles, both in vacuum (\(\sim 10^{-6}\) Torr) and at atmospheric pres-
sure. Figures 5(a) and (c) demonstrate that there is an order of magnitude current-level separation after ±50 V gate pulses and that the memory window (which is the separation between the two current levels) is kept constant after two hundred cycles (figures 5(b) and (d)).

The device displays better performance under N₂ atmosphere, with more separated current levels. This suggests that annealing in selected gas environments can be a valid pretreatment in the fabrication of MoS₂ encapsulated devices, such as the ones covered by Al₂O₃ [37], which are obviously more suitable for practical memory applications.

Conclusions

We have presented the electrical transport characterization of FET with monolayer MoS₂ channel. The conductance shows an n-type behavior, with prevailing on-state over a wide voltage range and an intrinsic hysteretic behavior. Hysteresis has been investigated as a function of the range and the sweeping rate of the hysteresis correlated with the adsorption energy of the system. Finally, we have confirmed the suitability of MoS₂ transistors as memory devices, especially when gases are stably adsorbed on the channel.

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Conflicts of interest

The authors declare no conflict of interest.

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