1. Introduction

Molecular hydrogen (H$_2$) has great potential as a nonpolluting source of energy used in several industrial applications. Especially it is used for desulphurization of petroleum products, synthesis of ammonia, methanol, and as a green fuel in mobile applications such as cars and rockets.$^{[1]}$ For these reasons, areas involving H$_2$ generation, storage, and detection are under continuous development. In special, sensing of H$_2$ is crucial for safety applications due to its flammability range of 4.0–75.0% by volume in the air.$^{[1,2]}$ Hence, it is indispensable to develop high-performance sensors with a wider measurement range (1–99% v/v H$_2$) to detect and monitor H$_2$ for industrial and safety applications.$^{[2]}$ There are several commercially available hydrogen sensors classified by the sensing mechanism like electrochemical, catalytic, work-function-based, and resistance-based.$^{[1]}$ However, most of these sensors present limitations that need to be overcome to satisfy the requirements for specific applications. For example, gas chromatography and mass spectroscopy are usual systems for H$_2$ detection that have an inherent drawback of large hardware size, requiring expensive and constant maintenance.$^{[1,2]}$ Resistive H$_2$ sensors based on metal oxide semiconductors generally operate at high temperatures (between 453 and 723 K) and need a fraction of oxygen in the ambient to detect H$_2$.$^{[1,3]}$ For this reason, there is an increasing demand for the development of H$_2$ sensors that are compact, operate at room temperature, with low cost and improved performance.

Recently, 2D layered materials have attracted scientific interest due to their properties such as high surface area, low electrical noise, and high electrical conductivity.$^{[4]}$ With considerable impact on gas sensor applications, 2D materials have their electric conductivity depending on the chemical state of their surface, which drastically changes under adsorption of gas molecules.$^{[4–6]}$ Such property, for instance, is exploited in graphene researches for detection of distinct gases such as NH$_3$,$^{[7]}$ NO$_2$,$^{[8]}$ CO$_2$,$^{[9]}$ and others. In this context, molybdenum disulfide (MoS$_2$) is one of the most promising transition metal dichalcogenides with great semiconducting properties, including a large intrinsic bandgap of 1.8 eV for the monolayer and high current on/off ratios.$^{[10,11]}$ Few-layer MoS$_2$ field effect transistors have been particularly successful for applications in nanoelectronics, optoelectronics and gas

This work presents a detailed experimental investigation of the interaction between molecular hydrogen (H$_2$) and monolayer MoS$_2$ field effect transistors (MoS$_2$ FET), aiming for sensing application. The MoS$_2$ FET exhibits a response to H$_2$ that covers a broad range of concentration (0.1–90%) at a relatively low operating temperature range (300–473 K). Most important, H$_2$ sensors based on MoS$_2$ FETs show desirable properties such as full reversibility and absence of catalytic metal dopants (Pt or Pd). The experimental results indicate that the conductivity of MoS$_2$ monotonically increases as a function of the H$_2$ concentration due to a reversible charge transfering process. It is proposed that such process involves dissociative H$_2$ adsorption driven by interaction with sulfur vacancies in the MoS$_2$ surface (V$_S$). This description is in agreement with related density functional theory studies about H$_2$ adsorption on MoS$_2$. Finally, measurements on partially defect-passivated MoS$_2$ FETs using atomic layer deposited aluminum oxide consist of an experimental indication that the V$_S$ plays an important role in the H$_2$ interaction with the MoS$_2$. These findings provide insights for future applications in catalytic process between monolayer MoS$_2$ and H$_2$ and also introduce MoS$_2$ FETs as promising H$_2$ sensors.
In fact, MoS$_2$ transistors have been used to monitor gases such as O$_2$, NO, NH$_3$, NO$_2$ and, in general, sensors based on few layers MoS$_2$ FETs exhibit advantages comparing with bulk sensors such as transparency, cost-effectiveness for massive production, and high sensitivity.[13,16,19] In terms of H$_2$ sensors by nonfunctionalized MoS$_2$ monolayer FETs (MoS$_2$ FET), the mechanism of detection has not been completely understood yet. Some works propose the H$_2$ detection mechanism that holds only for more complex structures like MoS$_2$ nanocomposites films doped with palladium (Pd),[26] platinum (Pt),[21] or heterojunctions of MoS$_2$ films and silicon.[22] Recently, Agrawal et al.[21] have shown a promising H$_2$ detection system using edge-oriented vertically aligned MoS$_2$ flakes in a 3D array without any doping, suggesting that bare MoS$_2$ has the potential for H$_2$ detection.

Here, we present a systematic study of the electronic properties of MoS$_2$ FETs under H$_2$ gas exposure. The MoS$_2$ sensors can detect a wide range of H$_2$ concentration (0.1% to up to 90%) as well as operate even at room temperature (300 K). These two characteristics are important for H$_2$ sensors in practical applications. Our results indicate that the H$_2$ reaction is independent of the choice of the substrate or metallic contacts. Based on our experimental data and previous density functional theory (DFT) studies, we suggest a model able to explain the electronic response of MoS$_2$ under interaction with H$_2$. We believe that H$_2$ molecules dissociate on the S vacancies ($V_S$) of MoS$_2$ transferring charge to MoS$_2$.[18–20] This report provides the H$_2$ detection mechanism that holds only for the presence of H$_2$ and the blue (upper) $I_{SD}$ versus $V_C$ curve corresponds to the saturation after 45 min of H$_2$ exposure ($I_{SD}^{Sat}$). The saturation criterion used here implies that the transfer curves became constant under H$_2$ exposure. The characteristics of the $I_{SD}$ versus $V_C$ curves in Figure 1b represents the typical n-type nature of the MoS$_2$ channel, which the current increase with the gradual increase in $V_C$ due to the accumulation layer of electrons.[11] This observation is consistent with previous works, which report that the MoS$_2$ transistor is predominantly n-type due to the spontaneous doping promoted by the sulfur vacancies.[27] Furthermore, note that the inset of Figure 1b shows a linear (ohmic) dependence of the $I_{SD}$ versus $V_{SD}$ curves without H$_2$ exposure, excluding the possibility of the Schottky barrier as the dominant transport mechanism.[11]

In all devices that we measured, the presence of molecular hydrogen causes a leftward shift in the $I_{SD}$ versus $V_C$ curves, with a simultaneous increase of the $I_{SD}$ current. This modulation of the MoS$_2$ conductivity indicates a strong response of the MoS$_2$ FET to H$_2$. This leftward shift means that is necessary a more negative

2. Results and Discussion

After thermal annealing for 12 h in ultrahigh pure Ar, we investigate the response of the MoS$_2$ FET supported on SiO$_2$/Si substrate for molecular hydrogen concentration ($[H_2]$) of 20% at 473 K. The optical image of the MoS$_2$ FET is shown in Figure 1a. We present the results at such temperature (473 K) because of the MoS$_2$ FET exhibit larger response to the H$_2$, where faster desorption of H$_2$ is also obtained, as discussed in detail along this work. Initially, we carried out source–drain current ($I_{SD}$) versus gate voltage ($V_G$) measurements at fixed source–drain voltage $V_{SD} = 1$ V for distinct H$_2$ exposure times, as shown in Figure 1b. The cyan (lower) $I_{SD}$ versus $V_C$ curve represents the standard current ($I_{SD}^{Init}$) without the presence of H$_2$ and the blue (upper) $I_{SD}$ versus $V_C$ curve corresponds to the saturation after 45 min of H$_2$ exposure ($I_{SD}^{Sat}$). The saturation criterion used here implies that the transfer curves became constant under H$_2$ exposure. The characteristics of the $I_{SD}$ versus $V_C$ curves in Figure 1b represents the typical n-type nature of the MoS$_2$ channel, which the current increase with the gradual increase in $V_C$ due to the accumulation layer of electrons.[11] This observation is consistent with previous works, which report that the MoS$_2$ transistor is predominantly n-type due to the spontaneous doping promoted by the sulfur vacancies.[27] Furthermore, note that the inset of Figure 1b shows a linear (ohmic) dependence of the $I_{SD}$ versus $V_{SD}$ curves without H$_2$ exposure, excluding the possibility of the Schottky barrier as the dominant transport mechanism.[11]

In all devices that we measured, the presence of molecular hydrogen causes a leftward shift in the $I_{SD}$ versus $V_C$ curves, with a simultaneous increase of the $I_{SD}$ current. This modulation of the MoS$_2$ conductivity indicates a strong response of the MoS$_2$ FET to H$_2$. This leftward shift means that is necessary a more negative
$V_C$ turn off the FET, which indicates an increase in the density of MoS$_2$ carriers after H$_2$ exposure. Besides, the conductivity change ($\Delta \sigma$) of the MoS$_2$ channel is expressed by the equation: $\Delta \sigma = \varepsilon \mu \Delta n$, where $\varepsilon$ is the electron charge, $n$ is the charge carrier density, and $\mu$ is the charge mobility. Thus, a conductivity increase can happen with an increase of charge carrier density or mobility or a combination of both. We discuss what is happening with these properties individually in more detail below.

In Figure 1c we plot the values of the threshold voltage ($V_{TH}$) in the left $y$-axis as a function of H$_2$ exposure time. The $V_{TH}$ is obtained by extrapolation of the linear region of the $I_{SD}$ versus $V_C$ curves presented in Figure 1b. Once the H$_2$ is introduced into the test chamber, $V_{TH}$ shifts toward negative voltages, indicating that a charge transfer process is taking place due to the H$_2$ adsorption. In this case, a fraction of the H$_2$ molecules donate electrons to the MoS$_2$ channel. Next, we shut off the H$_2$ gas (desorption process), and the threshold voltage returns to its initial value, recovering its condition without H$_2$ exposure ($V_{TH}^{INIT}$), indicating the reversibility of the process. The charge transfer process observed is different from what was reported by Agrawal et al.,$^{[21]}$ where the H$_2$ molecules receive electrons from MoS$_2$. However, our observation is consistent with other MoS$_2$ film sensors doped with Pd, Pt, and heterojunctions of MoS$_2$ films and silicon, which propose that hydrogen acts as a reducing agent donating electrons to the MoS$_2$.$^{[18,80-22]}$

The amount of charge per unit area transferred from hydrogen to the MoS$_2$ channel ($\Delta \sigma$) is shown in the right $y$-axis of Figure 1c. $\Delta \sigma$ is evaluated by the following equation $\Delta \sigma = \varepsilon \mu \Delta n = e \mu G \Delta n$, where $e = e \varepsilon_0 / d$ is the gate capacitance per unit area (12 nF cm$^{-2}$ for 285 nm of SiO$_2$), $e$ is the electron charge, and $V_{TH}^{INIT}$ is the threshold voltage under the H$_2$ exposure. Interestingly, the negative charge transfer from the H$_2$ molecules saturates in $= -4.5 \times 10^{11}$ cm$^{-2}$, suggesting that there is a limited number of active sites of the MoS$_2$ surface for the H$_2$ interaction. In addition, we show that the FET mobility ($\mu$) changes during H$_2$ exposure and desorption in Figure 1d. Noticeably, there is an enhancement of the FET mobility during the adsorption of hydrogen. We believe that such behavior may occur due to neutralization of charged impurities of the MoS$_2$ device under H$_2$ interaction, suggesting a reduction in the charge scattering mechanism. Thus, the conductivity increase in the MoS$_2$ FET is due to a combination of the increase of charge carrier density and mobility.

Further, we present a study of the MoS$_2$ FET response concerning molecular hydrogen concentration. Figure 1e shows a linear relationship between the device current ($\Delta I = I^{INIT}_{SD} - I^{REC}_{SD}$) and [H$_2$] in a semilog scale, using a fixed $V_{SD} = 1$ V and $V_C = -10$ V for 0.5%, 5%, 20%, 25%, and 50% of [H$_2$]. Such property can be used as a method to determine the [H$_2$] inside the test chamber. In Figure 1f we show the $I_{SD}$ versus time curve. Note that there is a considerably increase in $I_{SD}$ that is strongly related to the hydrogen concentration. Additionally, in the Supplementary Information, we present measurements for another MoS$_2$ FET in the range of concentrations spanning from 0.1% up to 90% of H$_2$. Hydrogen concentrations below 0.1% could not be measured due to limitations of our experimental setup. The mass flow controller used in our experimental setup does not produce reliable values for [H$_2$] below such amount. However, the device response indicates that the lower bound of the H$_2$ detection limit is actually lower than our reports. These results demonstrate that the MoS$_2$ FET is able to detect a large range of H$_2$ concentrations, as it is required for hydrogen sensors. Usually, the response time ($T_{REC}$) of a sensor is determined by the time required to reach 90% of the total conductance change under the gas exposure and the recovery time ($T_{REC}$) is the time necessary for the current to recover 90% of its ground state.$^{[20,22]}$ The minimal $T_{REC}$ is found to be $\approx 7$ min under 50% of H$_2$ (see Figure S1 in the Supporting Information), while the $T_{REC}$ is around 67 min for the same concentration. The response time of a sensor decreases for higher concentrations of hydrogen [H$_2$]. These high recovery and desorption times indicate that the H$_2$ interaction with the MoS$_2$ FET is limited by a diffusion reaction. This characteristic will be discussed in detail later.

Next, we show our investigation on the effects of temperature on the hydrogen detection with MoS$_2$ FETs. In Figure 2a, we show the MoS$_2$ FET sensor response (S) under [H$_2$] = 20% exposure from 300 up to 473 K. The sensor response rises up with temperature indicating that the process is thermally activated. Also, we observe a dependency of the device recovering time with temperature. The rate of desorption is slower at 300 K, compared to the rate of desorption at 473 K, meaning that desorption is also a thermally activated process, see Figure 2b. The inset in Figure 2b shows the recovery percentage of intrinsic properties of the MoS$_2$ FET (Rec) after 1 h of H$_2$ desorption as a function of the temperature, where the red curve is used only as a guide to the eyes. This data supports the reliability of the annealing of MoS$_2$ FET at 473 K for a couple of hours as an efficient method to speed up the system recovery. Also, thermal annealing is frequently used to restore gas sensors based in 2D materials.$^{[7,14]}$ The sensor response is generally defined as $S = (I^{REC}_{SD} - I^{INIT}_{SD}) / I^{INIT}_{SD}$.$^{[14,15]}$ The sensor response as a function of the temperature is obtained by $S = (I^{REC}_{SD} - I^{INIT}_{SD}) / I^{INIT}_{SD}$ curves measured with fixed $V_C = -10$ V. Nevertheless, the values of S retrieved in this configuration show the same behavior for other gate values.

For a better understanding of the reversibility of the process at 473 K, we carried out experiments with longer H$_2$ exposure times (see Figure S2 in the Supporting Information). We observe that for 473 K, the MoS$_2$ FET operates reproducibly, showing the same response repeated times. The initial conditions are fully recovered after a couple of hours without H$_2$ interaction in all cases. Such full recovery indicates that neither permanent bonds nor defect creation occur between H$_2$ molecules and MoS$_2$. Indeed, we confirmed this assumption by performing Raman spectroscopy of the monolayer before and after H$_2$ exposure (Figure S3 in the Supporting Information). We do not observe any indication of structural changes or irreversible chemical bonding after exposing the devices to H$_2$, which should be detected by changes in the Raman spectrum.$^{[28]}$ More precisely, no change of the Raman peaks $E_{2g}$ and $A_{1g}$ of the MoS$_2$ is observed.

Subsequently, we investigate the dependence of the sensor response with the applied gate voltage. Previous works showed that the response of sensors based in MoS$_2$ for O$_2$,$^{[14]}$ NO$_2$, and NH$_3$,$^{[16]}$ detection is improved in a given range of gate voltages. We also observed this behavior for hydrogen sensor response in our devices, as shown in Figure 2c. $S$ becomes remarkably higher for negative gates. The inset of Figure 2c shows that the $V_{TH}$ for this device is $\approx -16$ V, when the voltage approaches this
value, \( S \) increases rapidly. This means that the introduction of \( \text{H}_2 \) in the off-state of the transistor makes the current change more significantly than in the condition with the MOSFET initially in on-state.

Now, we show our investigation trying to elucidate how MoS\(_2\) FETs detect molecular hydrogen. In this context, we carry out experiments specifically designed to clarify: 1) If there is the detection of hydrogen at the MoS\(_2\)/metal interface. For example, there are \( \text{H}_2 \) sensors based on the modulation of the electrostatic properties of heterojunctions between the metal contact/2D materials and sensors based on the Schottky barrier effect.\(^1\)\(^,\)\(^2\)\(^,\)\(^16\)\(^,\)\(^29\)\(^–\)\(^31\) If the detection of \( \text{H}_2 \) depends on the underlying substrate. Previous reports have shown that oxygen gas could interact with graphene devices on SiO\(_2\)/Si substrates via the incorporation of \( \text{O}_2 \) molecules between the substrate and the graphene causing a change in its FET mobility.\(^32\) And, finally, if the \( \text{H}_2 \) detection is mainly related to intrinsic properties of MoS\(_2\). In this case, the mechanism is driven by dissociative adsorption of hydrogen at sulfur vacancies of MoS\(_2\).

We suspected that \( \text{H}_2 \) could interact with substrate defects and dangling bonds causing changes in MoS\(_2\) electronic mobility, such as those shown in Figure 1d. In this case, the mechanism is driven by the creation of only a few charge impurities, in contrast to the abundance of trap states that are present in the interface with SiO\(_2\)/Si substrates.\(^33\)\(^,\)\(^34\) We suspected that \( \text{H}_2 \) could interact with substrate defects and dangling bonds causing changes in MoS\(_2\) electronic mobility, such as those shown in Figure 1d. In this case, the mechanism is driven by the creation of only a few charge impurities, in contrast to the abundance of trap states that are present in the interface with SiO\(_2\)/Si substrates.\(^33\)\(^,\)\(^34\)

To check if there is the detection of hydrogen at the interface between MoS\(_2\) and the contact metal, or if the contact resistance changes under interaction with \( \text{H}_2 \), we perform measurements in two and four-probe (Hall bar) configurations. It is reasonable to assume that the total change in conductance (\( \Delta G \)) of MoS\(_2\) FET due to \( \text{H}_2 \) adsorption is represented by \( \Delta G = \Delta G_{\text{Channel}} + \Delta G_{\text{Contact}} \), where \( \Delta G_{\text{Channel}} \) is directly proportional to the carrier concentration injected in the channel and \( \Delta G_{\text{Contact}} \) is inversely proportional to the contact resistance change. Besides, it is known that the four-probe configuration eliminates the influence of contact resistance; in this case, we can detect only the change in conductance due to the charge transfer to the MoS\(_2\) channel (\( \Delta G = \Delta G_{\text{Channel}} \)). Therefore, if \( \text{H}_2 \) sensing is dominated by the contact resistance, i.e., \( \text{H}_2 \) molecules change the Schottky barrier height via modulation of the metal work function, we would not expect to measure a significant hydrogen response in a four-probe configuration.

Figure 3a shows the sensor response as a function of the \( \text{H}_2 \) exposure measured in two and four-probe configurations, represented by the black and green curve, respectively (more details are provided in the Supporting Information). Since \( S \) exhibits the same magnitude for both configurations, we infer that the sensing mechanism does not depend on the electrostatic configuration at the MoS\(_2\)/metal contact interface. This is also an expected result since our Au/MoS\(_2\) contacts have ohmic behavior as depicted in the inset of Figure 1b.

Next, we consider the influence of the underline substrate on the \( \text{H}_2 \) detection by MoS\(_2\) FETs. Trying to understand the role of the substrate in the hydrogen response, we produced a device with MoS\(_2\) supported on h-BN. The h-BN has an inert and flat surface that enables the creation of only a few traps. For example, there are \( \text{H}_2 \) sensors based on the modulation of the electrostatic properties of heterojunctions between the metal contact/2D materials and sensors based on the Schottky barrier effect.\(^1\)\(^,\)\(^2\)\(^,\)\(^16\)\(^,\)\(^29\)\(^–\)\(^31\) If the detection of \( \text{H}_2 \) depends on the underlying substrate. Previous reports have shown that oxygen gas could interact with graphene devices on SiO\(_2\)/Si substrates via the incorporation of \( \text{O}_2 \) molecules between the substrate and the graphene causing a change in its FET mobility.\(^1\)\(^,\)\(^2\)\(^,\)\(^16\)\(^,\)\(^29\)\(^–\)\(^31\) We suspected that \( \text{H}_2 \) could interact with substrate defects and dangling bonds causing changes in MoS\(_2\) electronic mobility, such as those shown in Figure 1d. In this case, the mechanism is driven by the creation of only a few charge impurities, in contrast to the abundance of trap states that are present in the interface with SiO\(_2\)/Si substrates.\(^33\)\(^,\)\(^34\)

Figure 2. Sensing performance of MoS\(_2\) FET for a fixed \( \text{H}_2 \) concentration of \( [\text{H}_2] = 20\% \) and \( V_{\text{SD}} = 1\, \text{V} \). a,b) The data were taken at a fixed \( V_G = -10\, \text{V} \). a) Sensor response (\( S \)) of MoS\(_2\) FET as a function of temperature: from 300 up to 473 K. b) Comparison of sensor response as function of time under the \( \text{H}_2 \) exposure (\( \text{H}_2 \) ON) at 300 K (blue curve) and 473 K (black curve). Inset: Recovery (Rec) percentage after one hour of \( \text{H}_2 \) desorption as a function of the temperature. c) Sensor response as a function of gate voltage at 473 K. Inset: \( I_{\text{SD}} \) versus \( V_G \) curve of the MoS\(_2\) transistor.
previously shown, $S$ depends on the gate voltage. These results reveal that the sensor response is nearly the same for both substrates, providing strong evidence that the sensing mechanism does not involve possible interactions between $H_2$ molecules with the underlying substrate. A more complete overview of MoS$_2$ FET supported on h-BN interaction with $H_2$ is found in Figure S5 (Supporting Information). All fabricated devices present the same sensor response as a function of temperature and $H_2$ concentration as the MoS$_2$ supported on SiO$_2$/Si.

Based on the analysis presented above, we can assert that the $H_2$ sensing mechanism occurs in the MoS$_2$ main channel. Therefore, at this point, we need to elucidate how the interaction of $H_2$ with the MoS$_2$ results in the conductance change of the MoS$_2$ in a reversible process. Some hypothesis can be drawn to explain the conductivity enhancement based in previously reported studies.$^{[15,16]}$ The main mechanism proposed here is the dissociative adsorption of hydrogen facilitated by the catalytic properties of MoS$_2$, as illustrated in Figure 4. The $A_G$, in this case, is driven by the charge transfer mechanism from $H_2$ molecules to the MoS$_2$ channel, represented by the following $H_2$ reaction: $H_2 \rightarrow 2H^+ + 2e^-$. In this scenario, absorbed $H$ atoms donate electrons to the conduction band of MoS$_2$, producing the sensor response. Theoretical and experimental works report that the existence of $V_S$ increase the catalytic activity of MoS$_2$. These references show that the hydrogen evolution is effectively improved due to the creation of $V_S$ in the monolayer MoS$_2$. $^{[37,38]}

Now we discuss in details the $H_2$ dissociative adsorption regarding absence and presence of sulfur defective sites in the MoS$_2$ surface. If a perfect MoS$_2$ monolayer is considered, $H$ atoms can bond to the sulfur atoms or molybdenum atoms after $H_2$ dissociation. Theoretical works show that $H$ atoms prefer to bond to sulfur atoms, presenting relatively lower energy concerning Mo atoms. The adsorbed $H$ atoms affect the electronic property of MoS$_2$, promoting a metallization of the surface due to the electron donation.$^{[24,36,39]}$ Yakovkin et al.$^{[39]}$ have investigated the relative instability of this bond, and suggested that some $H$ atoms can overcome the potential barrier for desorption and form $H_2$ molecules at high temperature.

On the other hand, DFT studies indicate that molecular hydrogen adsorption is more favorable in the MoS$_2$ surface if sulfur defective sites are present (Figure 4a), exhibiting a more effective energetic scenario than in a perfectly stoichiometric MoS$_2$ surface.$^{[24,25]}$ In accordance with other works that study the catalytic properties of MoS$_2$, in this case, after $H_2$ dissociation (Figure 4b), $H$ atoms bond to unsaturated molybdenum atoms$^{[25,26]}$ as illustrated in Figure 4c. Considering the arguments presented above, and the finding that $V_S$ is generated in the mechanical exfoliation carried out for the preparation of MoS$_2$ monolayers,$^{[40]}$ we suggest that the electron donation from the hydrogen molecules probably originates from the dissociative adsorption of $H_2$ due the presence of $V_S$. 

---

Figure 3. Influence of MoS$_2$ FET interfaces on the $H_2$ sensing mechanism. Sensing performance of MoS$_2$ monolayer transistor in a) and b) study for the $H_2$ concentration of $[H_2] = 20\%$ and 473 K. a) Comparison of MoS$_2$ FET sensor response in two-probe and four-probe (Hall bar) measurements. b) Sensor response versus threshold normalized voltage ($V_C - V_{TH}$) for MoS$_2$ FETs supported on SiO$_2$/Si and the h-BN substrate.

Figure 4. Representation of the dissociative adsorption of $H_2$ on the sulfur vacancy ($V_S$). a) The hydrogen molecule approaches to the MoS$_2$ surface. b) The dissociation of $H_2$ is induced by the presence of a sulfur vacancy. c) Adsorption of $H$ atoms in defective sites, forming $H$–Mo bonds.
To investigate the role of $V_S$ in hydrogen adsorption, we cover the MoS$_2$ surface with aluminum oxide (Al$_2$O$_3$) layers using atomic layer deposition (ALD) and monitor the response of such hybrid MoS$_2$/Al$_2$O$_3$ FET to H$_2$. Different coverages of Al$_2$O$_3$ are directly deposited on the top of the MoS$_2$ device at 373 K, using trimethyl aluminum (TMA) and H$_2$O precursors. Previous works showed that the Al$_2$O$_3$ grows preferentially on terrace edges and localized defects, where the covalent lattice is discontinued breaking the surface periodicity$^{[41,42]}$. Therefore, the Al$_2$O$_3$ clusters bind the intrinsic defects, including the $V_S$ in the MoS$_2$ monolayer. Based on the assumption that the sensor response depends on the dissociative adsorption of hydrogen in the $V_S$, we expect to see a lower sensitivity to H$_2$ molecules after the Al$_2$O$_3$ deposition. More details about the ALD steps to produce the MoS$_2$/Al$_2$O$_3$ FET and the AFM image before and after the Al$_2$O$_3$ grown are available in the Supporting Information.

In Figure 5a we show the ISD versus $V_G$ curves of a MoS$_2$ FET submitted to 5 growth pulses of Al$_2$O$_3$ and the bare MoS$_2$ device. This number of cycles was adopted to avoid the formation of an Al$_2$O$_3$ film on the MoS$_2$ device, solely promoting the passivation of $V_S$. The dotted curves represent the standard current, and the solid curves represent the current after 60 min of H$_2$ exposure at 473 K and [H$_2$] = 20%. According to these transfer curves, we observe that the current of MoS$_2$/Al$_2$O$_3$ FET (red curves), increases compared to the initial values for the bare MoS$_2$ FET (black curves). The FET mobility also increases from $≈$34–52 cm$^2$ V$^{-1}$ s$^{-1}$. This behavior is consistent with the dielectric screening effects from the Al$_2$O$_3$ overlayer observed in previous studies reported in the literature$^{[43]}$.

We should point out that we continue to observe H$_2$ interaction after the Al$_2$O$_3$ growth. Most importantly, we notice a reduction in the charge transfer from hydrogen to the MoS$_2$ channel, indicating a decrease in the number of active sites of the MoS$_2$ surface for the H$_2$ interaction. The charge transfer for the bare MoS$_2$ FET is approximately $n ≈ 7.4 \times 10^{11}$ cm$^{-2}$ while for the MoS$_2$/Al$_2$O$_3$ FET is $n ≈ 3 \times 10^{10}$ cm$^{-2}$. We estimate the charge transfer by the $V_{TH}$ shift obtained by the extrapolation of the linear region between $−17$ to $−20$ V for the ISD versus $V_G$ curves presented in Figure 5a. This behavior also occurs for devices in which a large amount of Al$_2$O$_3$ pulses is used.

To demonstrate the reduction of the MoS$_2$ reactivity to H$_2$ after the Al$_2$O$_3$ growth, we present in Figure 5b the current gain ($I_{TH}/I_{SD}$) as a function of the threshold voltage difference ($V_C − V_{TH}$), this normalization again was adopted because $V_{TH}$ changes drastically after the oxide growth. The current gain is lower for the MoS$_2$/Al$_2$O$_3$ hybrid device represented by the red curve in Figure 5b than the bare MoS$_2$ device (black curve). Besides, $I_{TH}/I_{SD}$ for MoS$_2$/Al$_2$O$_3$ FET is close to 1, indicating a small increase in current compared to its initial value without H$_2$ exposure. Additionally, the inset in Figure 5b shows the $S$ decrease after the Al$_2$O$_3$ growth. Such reductions in the current gain and sensor response demonstrate partial passivation of the reactive sites to hydrogen dissociative adsorption in the monolayer, evidencing that the $V_S$ play an important role in the H$_2$ interaction with the MoS$_2$. A similar decrease of the sensitivity of the H$_2$ detection system using edge-oriented vertically aligned MoS$_2$ flakes was observed after the passivation of the edges using ZnO films.$^{[23]}$

Nonetheless, MoS$_2$ interaction with hydrogen continues to occur even after Al$_2$O$_3$ growth. Since H$_2$ is a small molecule and can reach both sides of the MoS$_2$ sheet (top and bottom side), one cannot disregard that hydrogen also interacts with the bottom side of the MoS$_2$ layer, producing the hydrogen response. This observation is also consistent with the high response and desorption times obtained for the MoS$_2$ FET sensors. The top
side and bottom side of the monolayer are not equally accessible to H₂ molecules. Thus, two different mechanisms of interaction occur (see Figure S7 in the Supporting Information). We believe that the fast increase (decrease, in case of the desorption process) of the current is explained by the reaction of H₂ with the top of the monolayer, while the longer response time for current saturation (or recovery) is explained by the diffusion of H₂ molecules in between MoS₂ and the substrate. Furthermore, the even higher H₂ desorption time in comparison with the H₂ adsorption time is related with the state of the “trapped” H₂ molecules in between the MoS₂ and the substrate having more difficult to be desorbed. Interestingly, the response and recovering time in the MoS₂/Al₂O₃ FET is longer than the bare MoS₂, as shown in the red curve of Figure 5c. This result is consistent with mostly the diffusion of hydrogen between the MoS₂ sheet and the SiO₂/Si substrate, and the attenuation of the fast adsorption mechanism at the top of the monolayer.

Therefore, we believe that the sensor performance can be enhanced by the increase of Vₛ on the MoS₂ surface. For instance, Donarelli et al.[44] proposed the creation of sulfur vacancies of MoS₂ by thermal annealing in an ultrahigh vacuum. Based on this work, we performed an experiment to asset the effect of different treatment temperatures at inert Argon atmosphere in the H₂ sensor response. Such measurements reveal that the MoS₂ FET device treated at 473 K shows a higher response to H₂ then the one treated at 373 K. According our proposed H₂-sensing mechanism, this result indicates that a higher number of S vacancies is generated during the high temperature thermal treatment in agreement with the work of Donarelli et al. Such experiment adds an important evidence for the validation of our model based on the dissociative hydrogen adsorption catalyzed by vacancies. A more complete overview of this experiment is found in Figure S8 (Supporting Information).

Finally, our work shows that the modulation of the conductivity of the MoS₂ monolayer channel dominates the H₂ sensing process. We propose that such modulation originates from a charge transfer process associated with the dissociative H₂ adsorption. Such adsorption is a thermally activated process (as shown in Figure 2a) that is facilitated by the presence of Vₛ in the monolayer.[24,25] The effectiveness of Vₛ to induce the charge transfer reaction implies that there is a limited number of sites for the reaction to occur, corroborating our results of charge-transfer saturation, as shown in Figure 1c. After aluminum oxide passivation of the top side of the monolayer, we yet detect hydrogen, but the sensor response decreases. This result is a clear indication that the Vₛ plays an important role in the H₂ interaction with the MoS₂ and corroborates the idea that the gas molecule interacts with both sides of the MoS₂ sheet. An increase in the device mobility due to the H₂ presence is also observed that can be attributed to the screening of MoS₂ defective sites due to the hydrogen molecules adsorption. Besides, we believe that the existence of Vₛ can contribute to the instability of the hydrogen adsorption, corroborated by the reversibility behavior of the reaction.

3. Conclusion

We investigated the H₂ interaction with monolayer MoS₂ devices. Both the adsorption and desorption gas processes are strongly dependent on the temperature, and the sensing is independent of the choice of the substrate or metallic contacts. Our experimental data suggest that the charge transfer process from H₂ to the MoS₂ channel dominates the sensing process. We propose that the charge transfer originates from the dissociative H₂ adsorption, which is facilitated by the presence of Vₛ in the MoS₂. We also discussed evidence that the molecular hydrogen can interact on both sides of the MoS₂ sheet (top side and bottom side) based on our measurements of MoS₂/Al₂O₃ heterojunctions. Finally, we demonstrated that the MoS₂ device is a promising candidate for the development of molecular hydrogen sensors. The MoS₂ sensor responds to a wide range of hydrogen concentrations, operates at relatively low temperatures and do not require the presence of catalytic metals dopants (Pd, Pt), and can be fully recovered. Our findings also provide insights for future applications in catalytic processes making use of monolayer MoS₂ FETs.

4. Experimental Section

Device Fabrication: To investigate the molecular hydrogen interaction with MoS₂ FET, several devices supported on two different substrates were produced: Si covered with 285 nm of SiO₂ (SiO₂/Si) and hexagonal boron nitride (h-BN). To obtain the monolayer MoS₂, mechanical exfoliation with scotch tape technique was used.[46] To prepare the MoS₂ FET supported on h-BN, first, the mechanically exfoliated h-BN flakes were directly transferred from the tape to the SiO₂/Si substrate. After that, the dry viscoelastic stamping technique was used to transfer the MoS₂ in the top of h-BN/SiO₂/Si flakes.[46] The metallic contacts of both device types were fabricated employing standard electron beam lithography and thermal metal deposition of Au (50 nm). Finally, a second lithography step and SF₆ plasma etching to define the MoS₂ device geometry were used.

In Situ Electrical Measurements: After fabrication, the MoS₂ FET was fixed on a chip holder and transferred into a chamber connected to an electrical measurement system. A heater was used to control the temperature inside the chamber in the range of 300–473 K. The H₂ flow was determined by a mass flow controller and dilution with ultrahigh pure argon (Ar) was used to obtain different H₂ concentrations. More details of the gas sensing system can be found in our previous work.[7] Before carrying out electrical measurements under hydrogen exposure, an annealing procedure was performed in all devices presented in this work in Ar atmosphere at 473 K for 12 h. This thermal treatment is known to promote the removal of contaminating gases and humidity.[7,11] The external DC source of a lock-in amplifier (SR830) was used to provide a source–drain voltage (VSD) and a Keithley K2400 source to provide a DC gate voltage (V_G). The current between the source and drain (I_SD) was collected by a preamplifier and measured by a Keithley 2000 Digital Multimeter.

Supporting Information

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

Acknowledgements

This work was supported by CAPES, Fapemig (Rede 2D), CNPq, and INCT/Nanomaterials de Carbono. The authors are thankful to Lab Nano at UFMG for allowing the use of atomic force microscopy and CT Nano at UFMG for the Raman measurements. The authors acknowledge S. L. M. Ramos for the Raman measurements and E. S. N. Gomes for helping with the Raman analyses. The authors also acknowledge M. S. C.
Mazzoni for helping with theoretical discussions about phenomenology. K.W. and T.T. acknowledge support from the Elemental Strategy Initiative conducted by the MEXT, Japan and JSPS KAKENHI Grant Number JP15K21722.

Conflict of Interest
The authors declare no conflict of interest.

Keywords
field effect transistors, gas interaction, hydrogen detection, monolayer MoS₂

Received: August 31, 2018 Revised: November 19, 2018 Published online: December 3, 2018