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Air Pressure, Gas Exposure and Electron Beam Irradiation of 2D Transition Metal Dichalcogenides

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Abstract: In this study, we investigate the electrical transport properties of back-gated field-effect transistors in which the channel is realized with two-dimensional transition metal dichalcogenide nanosheets, namely palladium diselenide (PdSe₂) and molybdenum disulfide (MoS₂). The effects of the environment (pressure, gas type, electron beam irradiation) on the electrical properties are the subject of an intense experimental study that evidences how PdSe₂-based devices can be reversibly tuned from a predominantly *n*-type conduction (under high vacuum) to a *p*-type conduction (at atmospheric pressure) by simply modifying the pressure. Similarly, we report that, in MoS₂-based devices, the transport properties are affected by pressure and gas type. In particular, the observed hysteresis in the transfer characteristics is explained in terms of gas adsorption on the MoS₂ surface due to the presence of a large number of defects. Moreover, we demonstrate the monotonic (increasing) dependence of the width of the hysteresis on decreasing the gas adsorption energy. We also report the effects of electron beam irradiation on the transport properties of two-dimensional field-effect transistors, showing that low fluences of the order of few e[−]/nm² are sufficient to cause appreciable modifications to the transport characteristics. Finally, we profit from our experimental setup, realized inside a scanning electron microscope and equipped with piezo-driven nanoprobe, to perform a field emission characterization of PdSe₂ and MoS₂ nanosheets at cathode–anode separation distances as small as 200 nm.

Keywords: 2D materials; field-effect transistor; electrical transport; hysteresis; field emission; gas adsorption

1. Introduction

The exceptional properties of two-dimensional (2D) materials have focused an enormous amount of research activity on developing next-generation devices in the field of electronics and optoelectronics [1]. Graphene had the merit of being the prototype of these 2D materials and it is extremely interesting as a transparent electrode, but, being a gapless semiconductor, has several drawbacks in its digital logic and optoelectronic applications [2]. In this context, transition metal dichalcogenides (TMDs), such as MoS₂, WS₂, WSe₂, PdSe₂, and many others, were recognized as valid candidates to be exploited in those fields, due to their physical and chemical properties, including a finite band gap tuned by the number of layers, the absence of dangling bonds, chemical stability, etc. [3–6].

In this study, we report a detailed investigation of the effects caused by pressure, gas type and electron beam irradiation on the electrical transport properties of back-gated field-effect transistors with PdSe₂ or MoS₂ nanosheets as conducting channels. We demonstrate that the conduction of the devices can be tuned from the *n*-type (dominant in a high vacuum) to the *p*-type by modifying the

gas pressure. In addition, the transfer characteristics are significantly modified by the gas absorption, showing a widening of the observed hysteresis.

Interestingly, we also show that the transport properties are clearly affected by electron bombardments at fluences as low as those typically involved in electron beam-based imaging and processing techniques. Finally, we report a characterization of the field emission properties of the nanosheets under investigation. Their *n*-type conduction as well as their high aspect ratio at the borders allow us to extract a current at the relatively low electric fields applied. These field emission properties open up new opportunities for the exploitation of 2D materials in vacuum electronics.

2. Materials and Methods

Back-gated field-effect transistors were fabricated on Si (highly *p*-doped)/SiO₂ (300-nm-thick) substrates with mechanically exfoliated PdSe₂ [7] and chemical vapor deposition (CVD) MoS₂ nanosheets [8,9]. The standard scotch tape method was applied to exfoliate single PdSe₂ crystals that had been synthesized via a thermal process of compressed tablets of selenium and palladium powders, mixed in an atomic ratio of 2:1 and held in a quartz tube at 850 °C and 7.5 μTorr for 72 h. The thermal cycle was repeated twice, the second time after mixing the PdSe₂ tablets with Se powder in a mass ratio of 1:4.

MoS₂ nanoflakes were obtained by CVD in a three-zone tube furnace, purged with Ar gas for 15 min to minimize the O₂ content. S powder was located upstream in a zone heated to 150 °C, while the Si/SiO₂ substrate and the MoO₃ precursor were placed in a downstream zone of the furnace, heated to 750 °C. The deposition process lasted 15 min, after which the sample was cooled down rapidly.

PdSe₂ has a pentagonal and puckered structure (Figure 1a), while MoS₂ has a hexagonal and planar structure (Figure 1b) [10,11].

Figure 1. (a) Puckered pentagonal configuration of palladium diselenide (PdSe₂) and (b) hexagonal molybdenum disulfide (MoS₂). (c) SEM top-view image of (c) PdSe₂- and (d) MoS₂-based field-effect transistors, fabricated on Si/SiO₂ substrates. PdSe₂ is exfoliated while MoS₂ is obtained by chemical vapor deposition. The two processes yield different flake sizes.

Nanosheets for this study were initially identified by optical microscopy and then confirmed by Raman spectroscopy. Furthermore, scanning electron microscopy (SEM) and atomic force microscopy (AFM) were employed to characterize the nanosheets' lateral size and thickness. While exfoliated PdSe₂ nanoflakes were multilayers with thicknesses around 15 nm, MoS₂ nanosheets were mostly monolayer or bilayers with thicknesses below 1.3 nm. Details regarding the materials' fabrication and characterization have been reported elsewhere [7–9,12,13]. Electron beam lithography and a standard

lift-off process were used to realize Ti(5 nm)/Au(40 nm) metallic electrodes contacting the nanosheets. In Figure 1c,d, we report a top-view SEM image of a back-gated field-effect transistor fabricated using a PdSe₂ (MoS₂) nanosheet as the channel and Ti/Au leads as the metal contacts.

The electrical measurements were performed inside a scanning electron microscope chamber, equipped with piezo-driven nanoprobe connected to a Keithley 4200 SCS (a semiconductor parameter analyzer by Tektronix Inc, Beaverton, Oregon) working as multi-source-measurement units. Metal leads were used as the source and drain electrodes in a three-terminal configuration, the back gate being realized by the Si substrate. The fabrication of more than two top electrodes allowed us to characterize more than one transistor on the same nanosheet to verify the sample homogeneity.

3. Results and Discussion

The electrical characterization of the PdSe₂ back-gated field-effect transistor is reported in Figure 2. The drain-source current-voltage, I_{ds} – V_{ds} , output characteristics (Figure 2a), measured in a high vacuum and at room temperature, are linear and demonstrate the formation of a good ohmic contact between PdSe₂ and Ti. The I_{ds} – V_{gs} transfer curve, reported in Figure 2b, was measured by fixing a bias $V_{ds} = 100$ mV between the source and the drain, and sweeping the gate bias V_{gs} forward from -80 V to $+80$ V and then backward from $+80$ V to -80 V. The transfer curve has a hysteretic behavior, often observed in 2D material-based field effect transistors (FET), and it can be explained in terms of adsorbates on the channel surface, trap states in the dielectric or at the dielectric/channel interface or due to intrinsic defects [7,14–16]. In particular, trap states can be filled (or emptied) during the gate bias sweep and can participate in the gating effect, originating the hysteresis [17,18].

Figure 2. PdSe₂ back-gated FET characterization in high vacuum. (a) Output curves I_{ds} – V_{ds} ; (b) transfer curve I_{ds} – V_{gs} . Comparison of transfer curves of the same device at atmospheric pressure and at high vacuum: (c) transfer curve measured in high vacuum for a forward gate bias sweep (from -50 V to $+50$ V); (d) transfer curve measured at 760 Torr; (e) transfer curve measured after keeping the transistor at 760 Torr for 8 h; (f) transfer curve measured in high vacuum again.

The measured curve shows a clear ambipolar behavior and a current modulation of about one order of magnitude. The observed ambipolar behavior gives an indication that we are dealing with a semiconducting material characterized by a small band gap. We note that the band gap amplitude is expected to depend on the number of layers. According to the nanosheet characterization, the PdSe₂ layer under investigation is about 15-nm thick, i.e., about 25 layers [10], which should correspond to a bandgap less than 100 meV [19]. The transfer curve reported in Figure 2b shows a conductance minimum at about $V_{gs} = 0$ V that is indicative of the midgap alignment of the Fermi levels of the contacts. These curves also allowed us to obtain an estimation of the field-effect mobility, using the following equation:

$$\mu = \frac{L}{W} \left(\frac{1}{C_{SiO_2} \cdot V_{ds}} \right) \cdot \frac{dI_{ds}}{dV_{gs}} \quad (1)$$

where L and W are the channel length and width, respectively, and C_{SiO_2} is the capacitance per unit area of SiO₂. We can calculate $C_{SiO_2} = \frac{(\epsilon_0 \cdot \epsilon_{SiO_2})}{t_{SiO_2}} = 0.11 \cdot 10^{-3} \text{ F/m}^2$, considering that ϵ_0 is the vacuum permittivity, $\epsilon_{SiO_2} = 3.9$ is the relative permittivity of SiO₂ and $t_{SiO_2} = 300 \text{ nm}$ is the thickness of SiO₂. Then, evaluating the slope $\frac{dI_{ds}}{dV_{gs}}$ of the $I_{ds} - V_{gs}$ curve in the linear region, we obtain the field-effect mobility, $\mu \approx 3.0 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, within the range of values typically reported ($0.01\text{--}100 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$) for TMD-based FETs on SiO₂ [20–25]. In Figure 2c–f, we report the evolution of the transfer characteristics measured in the presence of different pressure conditions, i.e., at atmospheric pressure and in a high vacuum (10^{-6} Torr), in order to verify the effects of the pressure on the transistor properties. We first show the curve measured in a high vacuum (Figure 2c) and then the curve measured at 760 Torr (Figure 2d). The pressure was raised gradually by controlling the air flow via a high precision vacuum valve. We observe that the $I_{ds} - V_{gs}$ transfer curve shifts towards a positive bias that means a change from n -type to p -type conduction in the investigated gate bias range. By keeping the device exposed to air (atmospheric pressure) for about 8 h, the p -type behavior is further enhanced (Figure 2e), with no indication of ambipolarity. Successively, by reducing the pressure back to 10^{-6} Torr, we demonstrate (in Figure 2f) that the process can be reversed by restoring the ambipolar conduction centered almost at $V_{gs} = 0$ V. The reversibility of this phenomenon provides an opportunity to use the pressure as a controller to tune the conduction type from n to p or vice versa in PdSe₂ devices. However, it has been reported that long air exposure (>15 days) can result in the definitive suppression of n -type conduction [26]. The observed reversible conduction type can be due to the activated chemisorption of molecular O₂, probably in the Se vacancies, and desorption by vacuum annealing [7,26].

A similar characterization of the effect of pressure on the transport properties of 2D field-effect transistors was performed on monolayer MoS₂-based devices. In Figure 3a, we report the $I_{ds} - V_{ds}$ output characteristics, measured for different values of the gate voltage. The experimental data evidence a clear modulation of the current up to five orders of magnitude and an asymmetric behavior. Usually, the Fermi level at the metal–MoS₂ interface is pinned above the midgap of MoS₂ by either a metal work function modification due to interface dipole formation or by the production of gap states owing to the intralayer S–Mo bonding being weakened by metal [27]. As a consequence of the Fermi level pinning, Schottky barriers are formed at the contacts, causing the small rectification observed in the output curves as well as a dominant n -type behavior [9,28,29].

Figure 3. Electrical characterization of a monolayer MoS₂ field-effect transistor. (a) I_{ds} – V_{ds} output characteristics measured in a high vacuum for various gate bias values. (b) I_{ds} – V_{gs} transfer characteristic measured in a high vacuum. (c) Evolution of the transfer characteristics from vacuum to atmospheric pressure of Ar or H₂. (d) Evolution of the transfer characteristics from vacuum to atmospheric pressure of O₂, N₂, and CH₄.

In Figure 3b we show a I_{ds} – V_{gs} transfer curve, measured in a high vacuum (10^{-6} Torr) and at room temperature, by applying a bias $V_{ds} = 100$ mV. We note that the device has the expected *n*-type conduction and clear hysteresis. In addition, we estimate a field-effect mobility of about $1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and an on-off ratio of about six orders of magnitude. The I_{ds} – V_{gs} transfer curves at atmospheric pressure (Figure 3c,d) were then measured by filling the SEM chamber with selected gases. We observe that the exposure to gas provokes significant modifications of the curves, in particular causing a reduction in the conductance and/or a widening of the hysteresis. More precisely, we stress that when monolayer MoS₂ FET is exposed to argon or hydrogen atmospheric pressure, the main effect is the enlargement of the hysteresis, keeping the same conductance values at the maximum (positive and negative) gate bias (Figure 3c). On the other hand, when oxygen, nitrogen, and methane are employed, a reduction in the conductance is also observed (Figure 3d). In all cases, the device remains in the *n*-type conduction due to the intrinsic doping of MoS₂ by S vacancies and to the pinning effect [27,30]. Moreover, S vacancies and other defects like unreacted MoO₃ play a role as centers for gas adsorption [8], favoring charge trapping and an increase in the hysteresis.

From the curves of Figure 3c,d, we can obtain the relation between the hysteresis width, H_w (here defined as the V_{gs} difference at 10 pA current) and the gas adsorption energy E_{ads} [31–33]. The results are summarized in Table 1. E_{ads} are ordered for increasing absolute value to evidence the monotonic dependence of H_w on E_{ads} .

Table 1. Summary of the hysteresis width, H_w , extracted from the transfer curves of Figure 3c and 3(d) for the various gases, with the indication of the gas adsorption energy E_{ads} . E_{ads} , which is negative, is obtained by DFT calculations assuming that $E_{ads} = E_{MoS_2+gas} - E_{MoS_2} - E_{gas}$, with E_{MoS_2+gas} the total energy of the system, E_{MoS_2} the energy of MoS_2 and E_{gas} the gas phase molecules [31–33].

	Vacuum	Ar	H ₂	O ₂	N ₂	CH ₄
$ E_{ads} $ (meV)	1	1	70	106	114	407
H_w (V)	12.4	25.4	31	39.4	40.9	51.0

To complete the characterization of the transport properties in $PdSe_2$ - (Figure 4a) and MoS_2 -based (Figure 4b) field-effect transistors, we also investigated the effect of electron beam irradiation. Indeed, 2D materials are necessarily exposed to electron irradiation during fabrication or imaging processes, as in electron beam lithography or simply in SEM imaging. To measure such an effect, we performed an experiment in the SEM chamber using a 10 keV-electron beam to irradiate the nanosheets at various fluences. We clarify here that electrical measurements were performed soon after each irradiation (when the beam is switched off). The first I_{ds} - V_{gs} transfer curve was measured in its pristine state, before the irradiation, and was compared to the curves measured for successively increasing levels of fluences up to $4160 \text{ e}^-/\text{nm}^2$ for $PdSe_2$ (Figure 4c) and up to $100 \text{ e}^-/\text{nm}^2$ for MoS_2 (Figure 4d).

Figure 4. SEM image (top-view) of (a) $PdSe_2$ and (b) monolayer MoS_2 . Field-effect transistors used to study the effect of 10 keV electron beam irradiation on the transport properties of the transistors. (c) Transfer characteristics measured for various fluences for (c) $PdSe_2$ and (d) monolayer MoS_2 .

From the data in Figure 4c, we note that electron irradiation causes a suppression of the n -type conduction towards a p -type conduction. On the other hand, from Figure 4d, we see that n -type conduction is enhanced in the MoS_2 device. Comparing the two behaviors, it seems that electron irradiation acts with opposite modifications on $PdSe_2$ and in MoS_2 devices. Actually, it has been reported that effects on $PdSe_2$ may be irreversible [34], differing from MoS_2 , in which vacuum annealing

can restore its initial state [35]. To explain the experimental observations, we need to take into account that electron irradiation can easily produce Se and S vacancies, due to the small energy (less than 10 eV) necessary for the displacement of a chalcogen atom [36]. Vacancy formation is responsible for *p*-type conductivity, in particular when dealing with thick nanosheets (as in the case of 15-nm-thick PdSe₂), in which a larger beam energy can be adsorbed [34].

A further effect of electron irradiation is the formation of electron–hole pairs in both the SiO₂ oxide and the Si substrate. Therefore, holes may accumulate in the oxide (while electrons are easily transported away by the bias) causing a gating effect that increases the *n*-type doping. This process is dominant for MoS₂, where there is a limited release of energy and negligible S displacement because of the atomic thickness.

Our results are of interest to evaluate the radiation hardness of 2D materials to develop devices working in high radiation environments (such as space or nuclear plants).

Finally, we also performed a complete field emission characterization of PdSe₂ and MoS₂ nanosheets, to profit from the sharp edges of 2D materials as well as from a work function that, in these materials, decreases with the decreasing number of layers [37] (4.3 eV in monolayer PdSe₂ [19] and about 4.4 in monolayer MoS₂ [38]). The high aspect ratio and the low work function are desirable parameters to extract electrons from a material by means of an external electric field (field emission). The main interest in field emission is in the vacuum electronics context, in electrically operated floating gate memory cells or displays in electron and X-ray sources [39–43].

The most widely accepted theoretical framework to describe the field emission (FE) phenomenon was created by Fowler and Nordheim. They developed the so-called Fowler–Nordheim (FN) theory [44] based on a one-dimensional free electron model to calculate the tunneling probability through a triangular barrier. In this model, the FE current is written as:

$$I = S \cdot A \phi^{-1} \left(\beta \frac{V}{d} \right)^2 \exp \left[-B \phi^{3/2} \left(\beta \frac{V}{d} \right)^{-1} \right] \quad (2)$$

where *S* is the emitting surface, ϕ is the work function of the emitter, β is the field enhancement factor, V/d is the applied electric field (*V* is the applied voltage, *d* is the separation distance between the emitter and the anode), *A* and *B* are dimensional constants.

Field emission measurements, reported in Figure 5, were performed in the high-vacuum chamber of a scanning electron microscope equipped with piezo-driven metallic nanoprobe, for both PdSe₂ and MoS₂ nanosheets. In particular, we placed one probe on the metal electrode contacting the nanosheet (cathode emitter), while the second tip (anode) was positioned at a controlled (with nanometric precision) separation distance *d* from the emitter. The current-voltage, *I*–*V*, characteristics were then measured by performing a voltage sweep up to maximum 100 V (to avoid circuit failure) and recording the flowing current with a resolution better than 0.1 pA. The layout of the FE setup is shown in Figure 5a. The field emission *I*–*V* characteristic measured for a 4-nm-thick PdSe₂ sample is reported in Figure 5b. The experiment was performed by positioning the tip anode at *d* = 200 nm from the emitter surface. We could then evaluate the turn-on field *E*_{turn-on}, i.e., the field at which the current starts to raise exponentially, and we found that *E*_{turn-on} ≈ 80 V/μm, considering that *E*_{turn-on} = *V*/(*k*_{tip}·*d*), where *k*_{tip} = 1.6 is a correction factor to take into account the tip-shaped anode [45]. In addition, the field enhancement factor β can be evaluated from the slope *m* of the linear Fowler–Nordheim plot, $\ln(I V^{-2})$ vs V^{-1} , shown in Figure 5d, considering that $\beta = -B k_{tip} d \phi^{3/2} / m$, and we found $\beta = 44$ for the cathode–anode distance of 200 nm.

Figure 5. (a) Layout of the field emission measurement setup: a piezo-driven metallic nanoprobe is used as the anode and it is finely positioned at controlled distance from the nanosheet emitter. (b) FE current from PdSe₂ nanosheet at cathode–anode separation distance $d = 200$ nm. (c) FE current from MoS₂ monolayer at distance $d = 200$ nm. Fowler–Nordheim plots corresponding to the I–V curves of PdSe₂ (d) and of MoS₂ (e). Solid lines represent the linear fittings.

Similarly, FE characterization was performed on monolayer MoS₂ (Figure 5c) at a separation distance $d = 200$ nm.

The linear FN plot reported in Figure 5e confirmed the FE nature of the measured current. We found that the turn-on field is about $100 \text{ V}/\mu\text{m}$ and $\beta = 54$. The higher turn-on field is easily explained in terms of the higher work function, while the higher field enhancement factor may originate from the better aspect ratio of the emitter, the MoS₂ nanosheet being thinner than the PdSe₂ one. We note that the reported FE parameters are comparable with other widely investigated field emitters such as nanowires [46,47], carbon nanotubes [48,49] and nanostructures [50,51] measured in similar conditions.

4. Conclusions

The transport properties of two-dimensional PdSe₂ and MoS₂ back-gated field-effect transistors were investigated. We reported the transfer characteristics measured under different pressure conditions and gas types, demonstrating that the channel conductance is severely affected by the environment up to and including the possibility of reversibly tuning the conduction from the n - to the p -type or vice versa. Moreover, we showed that standard electron irradiation employed in electron beam lithography processes, as well as in SEM imaging, provokes the formation of defects in the 2D channel and causes a gating effect that significantly modifies the transistor properties. Finally, we also reported the field emission characterization of PdSe₂ and MoS₂ nanosheets, confirming their suitability for vacuum nanoelectronics applications.

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