PtSe$_2$ phototransistors with negative photoconductivity

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Abstract. Platinum diselenide (PtSe$_2$) is one of the most studied materials of the emerging group-10 transition-metal dichalcogenides. We investigate the electrical conduction and the photoconduction of PtSe$_2$ ultrathin films exploited as the channel of back-gated field-effect transistors. The channel resistance decreases with the rising temperature and shows that the films have semiconducting behaviour. The gate modulation confirms a p-type conductivity with field-effect mobility up to 30 cm$^2$/(Vs). Under exposure to the radiation from a super-continuous white light source, a reduction of the PtSe$_2$ electrical conductivity (negative photoconductivity) is observed in low vacuum, while a positive photoconductivity emerges only under high-power illumination conditions. Although, the positive photoconductivity arises from conventional photoconductive effect, the negative photoconductivity can be explained as the combination of the photogating effect caused by charge accumulation in the SiO$_2$ dielectric and the photo-induced desorption of adsorbates.

1. Introduction

Two-dimensional (2D) transition-metal dichalcogenides (TMDs) such as MoS$_2$, MoSe$_2$, WS$_2$, WSe$_2$, have been widely investigated over the last decade for their intriguing properties and possible applications [1–9]. They constitute a class of layered materials where each monolayer consists of an inner array of metal atoms covalently bonded and sandwiched between two arrays of chalcogens. The monolayers are weakly bonded by van der Waals forces to form the multilayer structure [10].

More recently, TMDs based on group-10 transition metals, represented by palladium (PdSe$_2$) or platinum (PtSe$_2$) diselenide and their disulfide analogues, have gained popularity for their useful electrical and optical properties [11–16]. The presence of d-electrons in the group-10 transition metals gives rise to additional semiconductor bands making the electrical and optical properties largely tunable by the number of layers [17].

In this paper, we focus on PtSe$_2$, a material that can offer easy integration in semiconductor technologies because of its production in 2D form by direct selenization of platinum films, deposited at rather low temperatures (400 °C). The PtSe$_2$ bulk, with slightly indirect overlap of the conduction and
valence bands, exhibits a semi-metallic nature that undergoes a semiconductor transition when it is thinned to a few atomic layers [18]. The monolayer has an indirect bandgap of ~1.2 eV that reduces to 0.3 eV for the bilayer. The bandgap of the multilayer structure is still not well known, although a theoretical bandgap ≤0.25 eV has been predicted for 2.5 nm thick PtSe$_2$ [15,18]. Such bandgap covers the energy range interesting for the telecommunications and the solar energy harvesting [19]. Moreover, the high mobility, theoretically limited to 4000 cm$^2$V$^{-1}$s$^{-1}$[20] and experimentally proven up to ~200 cm$^2$V$^{-1}$s$^{-1}$[21], might enable the fabrication of fast electronic devices.

In this paper, we investigate the electrical behavior of 3nm-thick PtSe$_2$ films over a wide temperature range demonstrating semiconducting p-type conduction, with reasonable gate modulation and relatively high hole mobility.

The white laser irradiation reveals an uncommon phenomenon. While for most of TMDs nanosheets light exposure induces an increase in the material conductivity because of charge carrier photogeneration [22,23], this effect is observed in PtSe$_2$ only under high light intensity and reduced air pressure. Indeed, light exposure provokes a reduction of the channel conductance, i.e. a negative photoconductivity, which can be explained by the combination of oxygen photodesorption and photogating effect due to charge accumulation in the SiO$_2$ dielectric.

2. Experimental section

Pt films of 0.7 nm, sputtered on Si substrates, were selenized in a two-zone furnace. Se pellets were evaporated for 2 hours in a zone at 220 °C and let react in the second zone containing the sputtered chips at 400 °C. The fabrication procedure, described in details in ref. [24], ensures the complete conversion of Pt in PtSe$_2$. The obtained PtSe$_2$ films were then transferred onto a SiO$_2$/Si substrate (85 nm) grown oxide on p-type silicon, ρ ~ 0.001 – 0.005 Ωcm and successively patterned using a photolithography mask and SF$_6$-based etching process. Finally, standard photolithography and lift off process were applied to define a pattern of four Ni/Au (20 nm/150 nm) metal contacts for two- or four-probe electrical measurements. A schematic of the device and a scanning electron microscope (SEM) image of it are shown in Figure 1(a) and 1(b), respectively. The thickness of the final PtSe$_2$ film, measured by a transmission electron microscope (TEM, is around 3 nm (inset of Figure 1(c)), corresponding to about 6 layers, given the 0.5 nm thickness of the single monolayer [25]. Such a measurement confirms that the selenization process increases the initial Pt film thickness by a factor of ~4 [13].

![Figure 1](image_url)

**Figure 1.** (a) Layout and measurement setup of the PtSe$_2$ back gate transistor; (b) SEM top view of the patterned PtSe$_2$ channel over SiO$_2$/Si substrate, contacted by Au/Ni leads used as the source and drain. (c) Raman characterization of the prepared PtSe$_2$ film, showing the characteristic PtSe$_2$ peaks at 176 cm$^{-1}$ and 205 cm$^{-1}$. The inset shows a TEM image of the PtSe$_2$ film confirming a 3 nm thickness.

The successful synthesis of the PtSe$_2$ was confirmed by the Raman spectrum reported in Figure 1(c) showing two peaks ($E_g$ ~ 176 cm$^{-1}$ and $A_{1g}$~205 cm$^{-1}$). The position and relative intensity of these modes are consistent with the synthesis of multilayer PtSe$_2$ [26].
The electrical measurements were carried out in a Janis Probe Station (ST-500) equipped with four nanoprobe connected to a Keithley 4200 SCS (semiconductor characterization system), under different temperatures and pressures. A scheme of the measurement setup of the back-gated transistor in common source configuration is shown in Figure 1(a). The metal contacts are used as the drain and source electrodes and the probe station chuck, connected to the silicon substrate, provides the gate voltage. We tested several devices with the same channel length (L) and width (W), fabricated from the same PtSe₂ sheet and simultaneously patterned. The electrical measurements were performed in air at room pressure or at 1 mbar and at different temperatures.

Furthermore, the photoresponse of the materials was tested under irradiation from a super-continuous white light source (NKT Photonics, Super Compact) with wavelength ranging from 450 nm to 2400 nm, and maximum intensity $100 \text{ mW/mm}^2$.

3. Results and discussion

3.1. Electrical characterization

We initially applied two- and a four-probe technique to measure the channel $I_{ds} - V_{ds}$ characteristics. As reported in Figure 2(a), the two methods gave the same result, indicating that the device has good ohmic contacts with negligible resistance. Therefore, we used the simplest two-probe setup for further electrical characterization. Figure 2(b) shows a decreasing channel resistance $R$ ($R = V_{ds}/I_{ds}$) when the temperature $T$ is raised from 100 K to 400 K revealing the semiconducting nature of the PtSe₂ nanosheet. The semiconducting behavior is confirmed by the $G-V_{gs}$ (with $G = 1/R$) transfer characteristic that decreases for positively growing gate voltage, revealing the p-type conduction of the channel (Figure 2(c)). The p-type doping of the PtSe₂ channel can be mainly attributed to O₂ adsorbates [27] as well as to Pt vacancies [18]; it is favored by the use of Ni contacts of which the Fermi level aligns to the top of the PtSe₂ valence band.

![Figure 2](image_url)

Figure 2. (a) $I_{ds} - V_{ds}$ output curves measured in two- and four-probe configurations. (b) Channel resistance $R$ as a function of temperature. (c) $G-V_{gs}$ transfer curve ($G = R^{-1} = I_{ds}/V_{ds}$ is the channel conductance).

We evaluated the field effect mobility from the transfer curves of several similar devices as $\mu = \frac{L}{W C_{ox} V_{ds} \frac{dI_{ds}}{dV_{gs}}}$ ($I_{ds}$ and $V_{ds}$ are the drain current and voltage, $C_{ox} = 3.11 \text{ nF/cm}^2$ is the SiO₂ capacitance per area, $L$ and $W$ are the channel length and width). We found that the mobility is around $30 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, for the device tested at room temperature and 1 mbar vacuum pressure. These mobility values are order of magnitude higher than the ones found for other TMDs [28] and up to 5 times higher than the mobility obtained for PtSe₂ devices fabricated with different techniques [13,21].
3.2. Photoresponse

The effect of light on PtSe$_2$ nanosheets was investigated by illuminating the device with a supercontinuous white laser, with light pulses of given time duration and intensity (Figure 3(a)).

Figures 3(b) shows the device channel current under fixed drain bias for switching light at the intensity of 30 mW/cm$^2$, in air at 1 mbar. After a sequence of 11 pulses, 1 min long, the laser is switched off and the current is monitored in dark. A reduction of the channel current is observed under each laser pulse (ON-pulse), a trend opposite to the usual current increase normally observed under light as an effect of electron-hole pair photo-generation [29–31]. We point out that current reduction is a reversible phenomenon as the device returns slowly to the pre-irradiation state when the light source is turned off.

The negative photoconductivity could be caused by a photogating effect due to charge trapping in the SiO$_2$ layer and light-induced oxygen desorption [32]. Holes photogenerated in the Si substrate and in the PtSe$_2$ channel can be trapped in the SiO$_2$ gate dielectric. As a result, the accumulation of a positive charge acts as a positive gate voltage that lowers the channel conductance of the p-type transistor. Simultaneously, electrons in O$_2$ (and perhaps H$_2$O) molecules, adsorbed over the PtSe$_2$ channel, can be excited by light into the channel. The neutralized O$_2$ molecules can be easily desorbed causing a decrease of the channel doping, hence of its conductivity. Both charge trapping and O$_2$ desorption decrease the current by a mechanism that is reversible with characteristic time depending on hole detrapping and O$_2$ adsorption.

Figure 3(c) shows the photoresponse to 2 min long laser pulses for four exposure sequences corresponding to increasing intensities, from 25% to 100% (i.e.100 mW/mm$^2$) of the total laser power. The measurements are performed at 1 mbar. At low light intensity, the current exhibits the same behavior as in Figure 3b. At higher intensities, although the general decrease of the channel conductivity is confirmed, a sudden increase of current can be observed when the light is switched on. Such an increase, corresponding to positive photoconductivity, is the common photoconductive effect due to electron-hole photogeneration [29,31]. Therefore, Figure 3(c) demonstrates that negative and positive photoconductivity, caused by photogating effect/O$_2$ photodesorption and photoconductive effect, respectively, can occur simultaneously. The photogating effect dominates at lower intensities while the photoconductive effect can become visible only at higher light intensities.

4. Conclusions

In conclusion, we investigated the electrical transport in PtSe$_2$ thin films used as the channel of back gated field effect transistors. The temperature dependence of the channel conductance and the transfer characteristic confirmed the semiconducting nature of the PtSe$_2$ films underlying a p-type conduction.
with mobility as high as \( \sim 30 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \) at room temperature. Exposure to light at air pressure as low as 1 mbar showed a dominant photogating effect and light induced desorption of adsorbates that cause a negative photoconductivity. The photoconductive effect resulting in positive photoconduction appeared only at very high illumination.

References

[1] Huang J, Yang L, Liu D, Chen J, Fu Q, Xiong Y, Lin F and Xiang B 2015 Large-area synthesis of monolayer WSe2 on a SiO2/Si substrate and its device applications Nanoscale 7 4193–8
[2] Urban F, Passacantando M, Giubileo F, Iemmo L and Di Bartolomeo A 2018 Transport and Field Emission Properties of MoS2 Bilayers Nanomaterials 8 151
[3] Di Bartolomeo A, Genovese L, Giubileo F, Iemmo L, Luongo G, Tobias Foller and Schleberger M 2018 Hysteresis in the transfer characteristics of MoS 2 transistors 2D Materials 5 015014
[4] Ornelas C D, Bowman A, Walmsley T S, Wang T, Andrews K, Zhou Z and Xu Y-Q 2020 Ultrafast Photocurrent Response and High Detectivity in Two-Dimensional MoSe2-based Heterojunctions ACS Appl. Mater. Interfaces 12 4674–82
[5] Giubileo F, Iemmo L, Passacantando M, Urban F, Luongo G, Sun L, Amato G, Enrico E and Di Bartolomeo A 2019 Effect of Electron Irradiation on the Transport and Field Emission Properties of Few-Layer MoS 2 Field-Effect Transistors J. Phys. Chem. C 123 1454–61
[6] Iemmo L, Urban F, Giubileo F, Passacantando M and Di Bartolomeo A 2020 Nanotip Contacts for Electric Transport and Field Emission Characterization of Ultrathin MoS2 Flakes Nanomaterials 10 106
[7] Urban F, Martucciello N, Peters L, McEvoy N and Di Bartolomeo A 2018 Environmental Effects on the Electrical Characteristics of Back-Gated WSe2 Field-Effect Transistors Nanomaterials 8 901
[8] Di Bartolomeo A, Urban F, Passacantando M, McEvoy N, Peters L, Iemmo L, Luongo G, Romeo F and Giubileo F 2019 A WSe2 vertical field emission transistor Nanoscale 11 1538
[9] Grillo A, Passacantando M, Zak A, Pelella A and Di Bartolomeo A 2020 WS2 Nanotubes: Electrical Conduction and Field Emission Under Electron Irradiation and Mechanical Stress Small 16 2002880
[10] Jawaid A, Nepal D, Park K, Jespersen M, Qualely A, Mirau P, Drummy L F and Vaia R A 2016 Mechanism for Liquid Phase Exfoliation of MoS2 Chem. Mater. 28 337–48
[11] Miró P, Ghorbani-Asl M and Heine T 2014 Two Dimensional Materials Beyond MoS 2 : Noble-Transition-Metal Dichalcogenides Angew. Chem. Int. Ed. 53 3015–8
[12] Di Bartolomeo A, Pelella A, Liu X, Miao F, Passacantando M, Giubileo F, Grillo A, Iemmo L, Urban F and Liang S-J 2019 Pressure-Tunable Ambipolar Conduction and Hysteresis in Thin Palladium Diselenide Field Effect Transistors Advanced Functional Materials 29 1902483
[13] Yim C, Passi V, Lemme M C, Duesberg G S, Ó Coileáin C, Pallecchi E, Fadil D and McEvoy N 2018 Electrical devices from top-down structured platinum diselenide films npj 2D Mater Appl 2 5
[14] Di Bartolomeo A, Urban F, Pelella A, Grillo A, Passacantando M, Liu X and Giubileo F 2020 Electron irradiation of multilayer PdSe2 field effect transistors Nanotechnology 31 375204
[15] Li L, Xiong K, Marstell R J, Madjar A, Strandwitz N C, Huang J C M, McEvoy N, McManus J B, Duesberg G S, Goritz A, Wietstruk M and Kaynak M 2018 Wafer-Scale Fabrication of Recessed-Channel PtSe 2 MOSFETs With Low Contact Resistance and Improved Gate Control IEEE Trans. Electron Devices 65 4102–8
[16] Di Bartolomeo A, Pelella A, Urban F, Grillo A, Iemmo L, Passacantando M, Liu X and Giubileo F 2020 Field Emission in Ultrathin PdSe2 Back-Gated Transistors Adv. Electron. Mater. 6 2000094
[17] Guo G Y and Liang W Y 1986 The electronic structures of platinum dichalcogenides: PtS$_2$, PtSe$_2$ and PtTe$_2$. J. Phys. C: Solid State Phys. 19 995–1008

[18] Ansari L, Monaghan S, McEvoy N, Coleáin C Ó, Cullen C P, Lin J, Siris R, Stimpel-Lindner T, Burke K F, Mirabelli G, Caruso E, Nagle R E, Duesberg G S, Hurley P K and Gity F 2019 Quantum confinement-induced semimetal-to-semiconductor evolution in large-area ultrathin PtSe$_2$ films grown at 400 °C npj 2D Mater Appl 3 33

[19] Yim C, McEvoy N, Riaizimehr S, Schneider D S, Gity F, Monaghan S, Hurley P K, Lemme M C and Duesberg G S 2018 Wide Spectral Photoresponse of Layered Platinum Diselenide-Based Photodiodes Nano Lett. 18 1794–800

[20] Huang Z, Zhang W and Zhang W 2016 Computational Search for Two-Dimensional MX2 Semiconductors with Possible High Electron Mobility at Room Temperature Materials 9 716

[21] Jiang W, Wang X, Chen Y, Wu G, Ba K, Xuan N, Sun Y, Gong P, Bao J, Shen H, Lin T, Meng X, Wang J and Sun Z 2019 Large-area high quality PtSe$_2$ thin film with versatile polarity InfoMat inf2.12013

[22] Di Bartolomeo A, Genovese L, Foller T, Giubileo F, Luongo G, Luca Croin, Liang S-J, Ang L K and Schleberger M 2017 Electrical transport and persistent photoconductivity in monolayer MoS$_2$ phototransistors Nanotechnology 28 214002

[23] Anh Nguyen D, Oh H, Thanh Duong N, Ho Bang S, Jun Yoon S and Jeong mun seok 2018 Highly Enhanced Photoresponsivity of a Monolayer WSe$_2$ Photodetector with Nitrogen-Doped Graphene Quantum Dots vol 10

[24] Yim C, Lee K, McEvoy N, O’Brien M, Riaizimehr S, Berner N C, Cullen C P, Kotakoski J, Meyer J C, Lemme M C and Duesberg G S 2016 High-Performance Hybrid Electronic Devices from Layered PtSe$_2$ Films Grown at Low Temperature ACS Nano 10 9550–8

[25] Zheng H, Choi Y, Baniasadi F, Hu D, Jiao L, Park K and Tao C 2019 Visualization of point defects in ultrathin layered 1T-PtSe$_2$ 2D Mater. 6 041005

[26] O’Brien M, McEvoy N, Motta C, Zheng J-Y, Berner N C, Kotakoski J, Elibol K, Pennycook T J, Meyer J C, Yim C, Abid M, Hallam T, Donegan J F, Sanvito S and Duesberg G S 2016 Raman characterization of platinum diselenide thin films 2D Mater. 3 021004

[27] Bartolomeo A D, Giubileo F, Romeo F, Sabatino P, Carapella G, Lemmo L, Schroeder T and Lupina G 2015 Graphene field effect transistors with niobium contacts and asymmetric transfer characteristics Nanotechnology 26 475202

[28] Pelella A, Kharsah O, Grillo A, Urban F, Passacantando M, Giubileo F, Lemmo L, Sleziona S, Pollmann E, Madauß L, Schleberger M and Di Bartolomeo A 2020 Electron Irradiation of Metal Contacts in Monolayer MoS$_2$ Field-Effect Transistors ACS Appl. Mater. Interfaces 12 40532–40

[29] Han Y, Zheng X, Fu M, Pan D, Li X, Guo Y, Zhao J and Chen Q 2016 Negative photoconductivity of InAs nanowires Phys. Chem. Chem. Phys. 18 818–26

[30] Bouricha B, Souissi R, Bouguila N, Jlidi D and Labidi A 2019 Positive and negative photoconductivity in sprayed β-In$_2$S$_3$ thin films Mater. Res. Express 6 116456

[31] Liu G Z, Zhao R, Qiu J, Jiang Y C and Gao J 2019 Negative photoconductivity under visible light illumination in LaAlO$_3$/SrTiO$_3$ heterostructures J. Phys. D: Appl. Phys. 52 095302

[32] Cadiz F, Robert C, Wang G, Kong W, Fan X, Blei M, Lagarde D, Gay M, Manca M, Taniguchi T, Watanabe K, Amand T, Marie X, Renucci P, Tongay S and Urbaszek B 2016 Ultra-low power threshold for laser induced changes in optical properties of 2D molybdenum dichalcogenides 2D Mater. 3 045008