Field Emission in Ultrathin PdSe₂ Back-Gated Transistors

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This study deals with the electrical transport in back-gate field-effect transistors with ultrathin palladium diselenide (PdSe₂) channels. The devices are normally-on and exhibit dominant n-type conduction at low pressure. The electron conduction of PdSe₂ nanosheets, combined with the sharp edge and the work function decreasing with the number of layers, opens up new applications in vacuum electronics. This work is the first experimental demonstration of field emission current from few-layer PdSe₂ and extends the plethora of applications of this recently isolated pentagonal layered material. Field-emission from PdSe₂ nanosheets is obtained with a turn-on field below 100 V μm⁻¹ and attains currents up to the μA.

1. Introduction

The material research of the last decade has been largely dominated by 2D transition metal dichalcogenides (TMDs), which have been explored for numerous applications in electronics, optoelectronics, sensors, catalysis, etc.[1–4] More recently, the TMDs based on noble metals of group 10, such as PtS₂, PtSe₂, PdS₂, and PdSe₂, have attracted considerable interest for the strong layer-dependent properties and interlayer interactions arising from the d-orbitals nearly fully occupied and the highly hybridized pₓ orbital of the interlayer chalcogen atoms.[5,6] Layer-dependent tunable bandgap, air stability, anisotropy, and relatively high carrier mobility are winning properties of such materials.[6]

PdSe₂ has been the first isolated layered material with pentagonal structure that is stable in air.[7,8] The monolayer has a puckered morphology where each Pd atom is coordinated with four Se atoms and exhibits an indirect bandgap of ≈1.3 eV that vanishes with the increasing number of layers up to the metallic behavior of the bulk material. Owing to the tunable and narrow bandgap, multi-layer PdSe₂ has been utilized for long-wave[9] or ultra-broadband[10] infrared photodetectors at room-temperature with highly sensitivity.[11–14] The visible-light optical absorption, combined with the carrier effective mass and mobility that change along different transport directions, indicate PdSe₂ as a good material for electron/hole separation, suitable for photovoltaic applications.[15,16] The carrier mobility in the order of 100 cm² V⁻¹ s⁻¹ or more has been demonstrated in field-effect transistors with ambipolar characteristics and dominant polarity tunable by pressure or chemical doping.[6,17] The low lattice thermal conductivity at room temperature enables promising thermoelectric applications.[18,19] Due to the high bandgap variability and air stability, 2D PdSe₂ nanosheets have been also successfully used as a saturable absorber for generation of Q-switched laser pulses.[20]

Motivated by the attractive properties and wide applications, we investigated 2D PdSe₂ nanosheets for field emission, that is, for electron extraction under the application of a high electric field. Field emission (FE) offers significant scientific interests in material science and is utilized for electron microscopy, electron spectroscopy, e-beam lithography as well as in vacuum electronics for displays and microwave generation or for X-ray tubes.[21–25] The extraction of electrons is favored from low work function metals or semiconductors (the work function that vanishes with the increasing number of layers.[11] Furthermore, FE from few-layer PdSe₂ nanosheets is still an experimentally unexplored phenomenon.

Owing to the high surface to volume ratio, the electronic and optoelectronic properties of PdSe₂ nanosheets, like any other 2D TMD materials, can be dramatically impacted by atmospheric surface adsorbates. In TMD based transistors, ambient molecules, such as O₂ and H₂O, preferentially adsorb to the...
chalcogen surface vacancies and act as hole doping as well as electron traps, which electrically deplete the transistor channel by withdrawing electrons from it. Most studies agree that oxygen produces the greatest effect and that selenides are more sensitive than sulfide to the adsorbed atmospheric species. A vacuum annealing for several hours, especially if at temperatures higher than 100 °C, can remove adsorbates and n-type dope the TMD channel thus improving the conductance and mobility. Similarly, encapsulation by Al2O3, HfO2, or Si3N4 deposited at high temperatures or after some pre-annealing, usually results in strong electron doping, reduced hysteresis and improved electronic performance.

In this work we characterize PdSe2 field-effect transistors focusing mostly on electric stress and air exposure and we report the measurement of the field emission current from exfoliated PdSe2 flakes. Besides its fundamental interest, our study suggests another promising application of 2D PdSe2.

2. Experimental Section

PdSe2 nanosheets were obtained from bulk PdSe2 single-crystals using the standard mechanical exfoliation method by adhesive tape. For the synthesis of bulk PdSe2, selenium powder (99.999%) and palladium powder (99.95%) were mixed in an atomic ratio of Se: Pd = 2: 1, compressed into tablets, and placed into a quartz tube sealed under 10⁻⁵ mbar. Collocated inside a muffled furnace, the quartz tube was gradually heated up and then kept to the synthesis temperature of 850 °C for 70 h. After natural cooling down of the furnace to room temperature, the obtained poly-crystalline samples of PdSe2 were mixed with Se powder in a mass ratio of PdSe2: Se = 1: 4 and sealed in another evacuated quartz tube to repeat the above high temperature annealing process.

The exfoliated nanosheets were transferred onto a substrate of degenerately doped p-type silicon covered with 300 nm thick SiO2. Optical microscopy was applied to select flakes with thickness of 15–20 nm which were subsequently contacted with 5/40 nm Pd/Au bilayers through electron-beam lithography, metal evaporation, and lift-off. The chemical composition of the nanosheets investigated by energy dispersive X-ray spectroscopy revealed a Pd: Se atomic ratio close to 1: 2, while X-ray diffraction and Raman spectroscopy confirmed a layered crystal structure along the c-axis, as reported elsewhere (the unit cell of PdSe2 is orthorhombic with space group Pbca).

The scanning-electron (SEM) and atomic-force (AFM) microscope images of a selected PdSe2 nanosheet contacted by several metal leads, at a distance of about 950 nm from each other, is shown in Figure 1. The AFM height measurements (Figures 1b,c) indicate a uniform ≈17 nm thick nanosheet,
which corresponds to \( \approx 40 \) atomic layers (assuming the theoretical monolayer thickness of 0.41 nm\textsuperscript{17}).

The electrical measurements were performed at room temperature and under controlled pressure inside a SEM chamber (ZEISS, LEO 1530). The samples were contacted using piezo-driven tungsten tips (W-tips) which are moved in steps of 5 nm and positioned in the desired location with the help of the SEM imaging. The W-tips are connected to a Keithley 4200 semiconductor analyzer system. For the electrical measurements a three-terminal configuration was used, with different combinations of the metal leads as the source and drain and the Si substrate as the back gate of a field-effect transistor (a schematic is shown in Figure 1d).

### 3. Results and Discussion

The linear and symmetric output curves \((I_{ds}-V_{ds}, \text{drain current versus voltage, for stepping gate voltage } V_{gs} \text{ in common source configuration})\) of Figure 2a, referred to contacts labelled 4 and 5, indicate ohmic contacts at low bias. Figure 2b shows a typical set of transfer curves \((I_{ds}-V_{gs}, \text{drain current versus gate voltage at a given drain bias})\) for the gate voltage swept back and forth over increasing ranges. The measurements were performed after keeping the sample at low pressure \((<10^{-6} \text{ Torr})\) for several days to help removing adsorbates such as O\textsubscript{2}, H\textsubscript{2}O, etc., which could strongly affect the PdSe\textsubscript{2} conductivity.\textsuperscript{28}

The device is in the on-state at zero gate, that is, behaves as a normally on transistor, and has a dominant n-type behavior. The n-type conduction of PdSe\textsubscript{2} can be attributed to intrinsic defects, such as selenium vacancies,\textsuperscript{28} whose presence is confirmed by the clockwise and widening hysteresis with the increasing gate bias range. The transistor has two orders of magnitude on/off ratio, indicative of a channel with low-bandgap material, and a negative threshold voltage, \(V_{th} = -15 \text{ V}\) for the forward sweep that increases up to \(V_{th} = 30 \text{ V}\) during the reverse sweep (Figure 2b). The voltage shift, corresponding to a large hysteresis of the transfer curves, is typical of 2D materials and is ascribed to charge trapping in intrinsic (structural) and extrinsic (adsorbates) defects as well as in the SiO\textsubscript{2} gate dielectric.\textsuperscript{35,38,39} The maximum field-effect electron mobility is \(\mu = \frac{1}{L W} \frac{dI_{ds}}{dV_{gs}} \approx 20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\) (here, \(L\) and \(W\) are the channel length and width, respectively, and \(C_{SiO_2} = 11 \text{ nF cm}^{-2}\) is the SiO\textsubscript{2} capacitance per unit area). The electron mobility in PdSe\textsubscript{2} has been shown to decrease with the increasing number of layers;\textsuperscript{7} the achieved value is consistent with that reported for devices with similar thickness.\textsuperscript{7,9,17}

Remarkably, Figure 2b shows the appearance of hole conduction (ambipolar behavior) for \(V_{gs} \approx -45 \text{ V}\). However, the limitation imposed to the maximum gate voltage to avoid SiO\textsubscript{2} breakdown prevented further characterization of the p-type conduction. To assess the repeatability of the reported behavior, we checked different contact combinations, finding similar results even when the channel included intermediate
floating metal leads (Figure 2c). Similarly, the comparison of the transfer characteristics for contacts 1–2 and 4–5, which correspond to transport along two perpendicular crystallographic axes, do not evidence any appreciable difference as the higher current between contacts 1–2 can be attributed to the larger and shorter channel.

In PdSe2 transistors, it has been recently shown that the exposure to air, for a time less than a week, changes the pristine n-type behavior of the device, by decreasing the n-type conduction and increasing the p-type conduction.\[4,28,40\] This air aging effect is arrested when the device is placed in vacuum, confirming that the change is caused by ambient exposure. Longer term air exposure leads to a complete suppression of the n-type conduction and a further increase in the p-type conduction.

We confirmed that the electrical behavior of PdSe2 is strongly influenced by the ambient, when at the end of our experiment we exposed the device to air. Figure 3a shows that the electron current gradually decreases and a clear ambipolar behavior appears after an overnight exposure to air, while the ohmic behavior of the contacts is maintained (Figure 3b). However, consistently with previous studies on the reversibility of short-term aging of PdSe2 in air,\[4,28,41\] Figure 3a shows that the air induced change is reversible: the device returns to its n-type dominant behavior after the re-establishment of the $10^{-6}$ Torr pressure.

The effect of adsorbed H2O, O2, and O on pristine and Se vacancies in single and multilayer PdSe2, has been previously clarified by first principles density functional theory (DFT) calculations.\[28\] The exposure to air causes activated chemisorption of O2 at Se vacancy sites, with activation energy and binding energy $\approx 0.85$ eV and 1.3–1.6 eV, respectively. According to the DFT results, the defect complex eliminates the selenium vacancy gap states near the conduction band, thereby causing an apparent shift of the Fermi energy towards the valence band consistent with the observed increased p-type conduction. This short term chemisorption is reversible with a long term vacuum exposure or a low temperature inert atmosphere anneal. Instead, longer air exposure can yield a complete suppression of the n-type conduction and a further increase in the p-type conduction, owing to dissociative O2 chemisorption/reaction where PdO2 is formed.\[28\]

The observed electrical behavior can be easily understood considering that the multilayer nanosheet has low bandgap around 0.1 eV or less\[7–9\] and that Pd has higher work function (5.20–5.95 eV)\[42,43\] than PdSe2 (5.16–5.20 eV for multilayers[11,12]). Consequently, as clarified by the schematic band diagrams of Figure 3c, for intrinsic n-type doping, there is a band bending that favors electron conduction at zero and positive gate; the application of a negative gate voltage suppresses the n-type conduction and enables hole conduction at higher negative gate biases.

We cannot rule out that a change in the low Schottky barrier at the contacts can contribute to the stitching from the n-type dominant behavior in vacuum to ambipolar behavior in air. Such a change has been observed in carbon nanotube transistors with Pd-contacts, in which it has been directly related to a variation of the metal work function of the electrodes.\[44,45\] When exposed to an electron accepting gas, such as O2 or N2, the work function of the metal contact increases.\[46–48\] Such an increases, which has been measured for instance on Pd leads exposed to electron accepting NO2 gas,\[48\] hampers electron injections and facilitates hole conduction.

Figure 3. a) Transfer characteristics measured between leads 4 and 5 in vacuum, after exposure to air and after pump-down to pressure $<10^{-6}$ Torr. b) Output characteristics in air after 8 h exposure to air. c) Energy band diagrams at different gate voltages.
Considering the sharp edges and taking advantage of the work function that decreases with the reducing number of layers down to \( \approx 4.30 \) eV for the monolayer,[11,12] the 2D form of PdSe\(_2\) can be a good candidate for FE applications. To investigate FE from few-layer PdSe\(_2\) nanosheets, we selected flakes protruding from the metal leads. Figure 4a shows an example of a flake emerging from lead 1 with thickness \( \approx 4 \) nm (about 10 layers) as measured by AFM. For the FE measurements, we positioned one of the W-tips on the metal lead (cathode) and approached the PdSe\(_2\) flake with the second W-tip (anode). The current–voltage (I–V) characteristic obtained between lead 1 and the anode W-tip at growing distances from the PdSe\(_2\) nanosheet showing the evolution from electric contact to FE regime. The substrate back-gate was grounded during all the above measurements. e,f) Fowler-Nordheim plots obtained from Equations (1) and (2) models.

**Figure 4.** a) SEM image of a PdSe\(_2\) nanosheet (cathode) protruding from metal lead 1 and the anode W-tip used for field emission measurements. b) I–V characteristic with the anode W-tip in physical contact with the PdSe\(_2\) nanosheet. The inset shows the I–V curve on linear scale. c,d) I–V curves with the anode W-tip at growing distances from the PdSe\(_2\) nanosheet showing the evolution from electric contact to FE regime. The substrate back-gate was grounded during all the above measurements. e,f) Fowler-Nordheim plots obtained from Equations (1) and (2) models.

to the formation of a low Schottky barrier between the W-tip and the PdSe\(_2\) nanosheet.[49] Despite the rough contacting, the I–V curve appears smooth and a current up to the \( \mu \)A can be attained at \( V = 60 \) V.

Starting from the contact condition, we retracted the anode W-tip to given distances from the edge of the PdSe\(_2\) nanosheet and we performed voltage sweeps up to 100 V, while monitoring the current. Figure 4c shows a typical sequence where from the contact condition (magenta curve) we retracted the anode tip to distances \( \approx 100 \) nm and \( \approx 310 \) nm (dark cyan and red curves, respectively). At \( d = 100 \) nm, the I–V behavior mimics the one of the contact condition: Likely, a sort of loose electric contact has
established between the flake and the tip as result of electrostatic attraction. Instead, at \( d = 310 \text{ nm} \) an exponentially growing current, typical of FE, emerges from the setup noise floor (obtained with the anode W-tip far away from the nanosheet) at \( V = 45 \text{ V} \). This voltage corresponds to a turn-on electric field \( E_{\text{on}} = \frac{V}{d} = 90 \text{ V/µm} \) (\( k = 1.6 \) is the tip correction factor to account for the spherical geometry of the tip\(^{[50,51]}\)). We repeated the same sequence, at a near location (the one shown in Figure 4a), with the anode tip in contact and at 70, 200, and 300 nm distances, respectively, confirming the appearance of FE with a turn-on electric field increasing from \( \approx 60 \text{ V/µm} \) at 70 nm to \( \approx 90 \text{ V/µm} \) at 350 nm. We did not observe any apparent modification of the PdSe\(_2\) nanosheet after the FE measurements.

Although recently challenged,\(^{[52]}\) the FE current is usually analyzed using the simplified Fowler-Nordheim (FN) equation:\(^{[53]}\)

\[
I = \frac{S}{\Phi} \frac{E^2}{\Phi} \exp\left(-\frac{b \Phi^{3/2}}{E_s}\right)
\]

(1)

where \( \Phi (\text{eV}) \) is the work function of the emitting material, \( S(\text{µm}^2) \) is the emitting area, \( E_s (\text{V/µm}) \) is the local electric field, and \( a (1.54 \times 10^{-6} \text{ AV}^{-2} \text{ eV}) \) and \( b (6.83 \times 10^3 \text{ V m}^{-1} \text{ eV}^{-3/2}) \) are dimensional constants. The local electric field is \( E_s = \beta V/d \), where \( V \) is the applied potential, \( d \) is the cathode–anode distance, and \( \beta \) is the so-called field enhancement factor. Such a factor is related to the geometry of the cathode, with the sharper surfaces yielding the higher \( \beta \), and can attain values of several thousands.\(^{[24,54,55]}\) According to the FN theory, the slope of the straight-line fitting the \( \ln (I/V^2) \) versus \( 1/V \) FN plot can be used to estimate \( \beta \).

It has been recently suggested that when the material is very thin, but not necessarily 2D, due to discrete bound states, many basic assumptions of FN model become invalid and a modified FE scaling law should be used:\(^{[56]}\)

\[
I \propto \exp\left(-\frac{b \Phi^{3/2}}{E_s}\right)
\]

(2)

Figures 4e,f show Equation (1) and (2) fittings. The good agreement of both models with the experimental data at \( d_1 = 200 \text{ nm} \) and \( d_2 = 350 \text{ nm} \) provides evidence of the establishment of a FE regime but does not allow a clear discrimination between the two models. The magenta curve at a distance of 70 nm deviates from the linear behavior and is something in between FE and physical electric contact (dark cyan curve).

Using the data of Figure 4e, we can estimate a field enhancement factor of \( 5 \) at 200 nm and \( 40 \) at 350 nm, assuming \( \Phi = 4.70 \text{ eV} \) as the work function of the 4 nm flake.\(^{[10]}\) The increasing turn-on field and field enhancement factor with the anode–cathode distance is typical of nanoshaped emitters and has been discussed elsewhere.\(^{[157-60]}\) The field emission turn-on field is comparable and even better than we have previously reported for graphene (up to 600–1000 V µm\(^{-1}\))\(^{[62-64]}\) or other TMDs, such as MoS\(_2\) (up to 200 V µm\(^{-1}\))\(^{[65,66]}\) or WS\(_2\) (up to 140 V µm\(^{-1}\))\(^{[67]}\) under similar experimental conditions.

4. Conclusion

In summary, we have synthesized PdSe\(_2\) nanosheets that we have electrically characterized as the channel of back-gated field-effect transistors. In vacuum, the devices behave as normally-on n-type transistors with electron mobility \( \sim 20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \). A short exposure to air reversibly reduces the channel current and transforms the device conductance from n-type to ambipolar. We ascribed such an effect to charge trapping and doping by adsorbates, with a possible contribution of the variation of the Schottky barrier height at the contacts. Taking advantage of the intrinsic n-type conductivity, enhanced by the low pressure, of the sharp edges of flakes and of the layer-controllable work function, we have demonstrated that a high FE current up to the \( \mu \text{A} \) can be extracted from 2D PdSe\(_2\) nanosheets. Our study makes a step ahead towards the understanding and the application of PdSe\(_2\) in its 2D form, demonstrating that it can be suitably exploited as field emitter due to its relative low turn-on field, in similar conditions, with respect to graphene and MoS\(_2\).

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

ambipolar conduction, field-effect transistors, field emission, hysteresis, palladium diselenide

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