Highly Sensitive Electromechanical Piezoresistive Pressure Sensors Based on Large-Area Layered PtSe2 Films

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ABSTRACT: Two-dimensional (2D) layered materials are ideal for micro- and nanoelectromechanical systems (MEMS/NEMS) due to their ultimate thinness. Platinum diselenide (PtSe2), an exciting and unexplored 2D transition metal dichalcogenide material, is particularly interesting because its low temperature growth process is scalable and compatible with silicon technology. Here, we report the potential of thin PtSe2 films as electromechanical piezoresistive sensors. All experiments have been conducted with semimetallic PtSe2 films grown by thermally assisted conversion of platinum at a complementary metal–oxide–semiconductor (CMOS)-compatible temperature of 400 °C. We report high negative gauge factors of up to −85 obtained experimentally from PtSe2 strain gauges in a bending cantilever beam setup. Integrated NEMS piezoresistive pressure sensors with freestanding PMMA/PtSe2 membranes confirm the negative gauge factor and exhibit very high sensitivity, outperforming previously reported values by orders of magnitude. We employ density functional theory calculations to understand the origin of the measured negative gauge factor. Our results suggest PtSe2 as a very promising candidate for future NEMS applications, including integration into CMOS production lines.

KEYWORDS: Pressure sensors, platinum diselenide, two-dimensional, gauge factors, strain sensors

Layered two-dimensional (2D) materials have extraordinary electrical, optical, and mechanical properties that suggest high potential for a wide range of nanoelectronics applications.1,2 2D transition metal dichalcogenides (TMDs) have recently been intensively investigated due to their wide range of inherent electronic properties that complement graphene. Out of this family, platinum diselenide (PtSe2) is a relatively new and thus little explored TMD material. Monolayer PtSe2 is a semiconductor with a band gap of 1.2 eV3 while bulk PtSe2 becomes semimetallic with zero band gap.4,5 It has been grown epitaxially or synthesized on insulating substrates using thermally assisted conversion (TAC) of predeposited platinum (Pt) films by a vaporized solid selenium precursor.4,7 The latter process can be carried out at temperatures between 400 and 450 °C, which is compatible with standard semiconductor back-end-of-line (BEOL) processing,8 in contrast to other 2D materials.9–11 We have demonstrated potential applications of TAC-grown PtSe2 in highly sensitive gas sensors and photodetectors with equal or even superior performance.
compared to graphene and other TMD-based devices.\textsuperscript{7,12} Furthermore, top-down structured electrical devices with PtSe\textsubscript{2} have been demonstrated.\textsuperscript{13} Here, we explore the electro-mechanical properties of PtSe\textsubscript{2} in nanoelectromechanical system (NEMS) pressure sensors. The devices utilize the piezoresistive effect in PtSe\textsubscript{2}, which gives rise to a change in its

Figure 1. As-grown PtSe\textsubscript{2} film characterization: (a) AFM measurement of the selenized 1 nm initial Pt film including height profile of the step between the Si/SiO\textsubscript{2} substrate to the PtSe\textsubscript{2} film. (b) High-resolution AFM measurement displaying the RMS roughness. (c) Raman spectrum of the as-grown 4.5 nm thick PtSe\textsubscript{2} sample.

Figure 2. Pressure sensor fabrication and measurement. (a) Optical micrograph of one device with Au contacts and the PtSe\textsubscript{2} channel across the cavity area. (b) Schematic cross-section of the cavity area with suspended PtSe\textsubscript{2}. (c) Schematic of one device including contacts and cavity area. (d) Raman point spectrum of the PtSe\textsubscript{2} membrane area and the Si substrate. (e) Raman tomography cross sections of one device with suspended PtSe\textsubscript{2} (device 3.2) and one with collapsed membrane (collapsed device). On the right are the corresponding optical micrographs of the cavity areas (device 3.2 and the collapsed device) as well as one other working device (device 3.3) and one device without cavity (device no cavity) as reference. (f) Resistance change in % for one pressure cycle (vented, pumped down to 200 mbar, vented) of the four devices shown in panel (e) (left y-axis) and pressure on the outside of the membrane (right y-axis).
electrical resistance upon mechanical strain. We investigate PtSe2 membrane-based pressure sensors and find sensitivities that are orders of magnitude higher than those of nanomaterial-based devices14−17 including graphene.18−20 Furthermore, we obtain an average negative gauge factor (GF) of −84.8 for PtSe2 from a bending beam setup. Detailed density functional theory (DFT) simulations reveal an increase in the density of states (DOS) at the Fermi level of bulk PtSe2, corroborating the experimentally observed piezoresistive properties.

Polycrystalline PtSe2 films with nanometer sized grains were grown on silicon/silicon dioxide (Si/SiO2) substrates by TAC at 400 °C of predeposited 1 nm thick Pt films (Figure S1 in the Supporting Information). Comprehensive characterization of layered PtSe2 thin films synthesized in this manner, including X-ray photoelectron spectroscopy and scanning transmission electron microscopy, is presented in our previous work.4,7 The thickness and roughness of the layers were determined by atomic force microscopy (AFM, Figure 1a,b). A thickness of 4.5 nm was found for the selenized 1 nm initial Pt film. Assuming an interlayer distance of 0.6 nm for PtSe2,21 this corresponds to 7−8 layers for the 4.5 nm thick PtSe2 film. The root-mean-square (RMS) roughness of the layer was 0.284 nm. The Raman spectrum of the PtSe2 film shows two sharp and prominent peaks corresponding to the Eg and A1g modes of the 1T phase, attesting the crystalline nature of the films (Figure 1c).3 After the film growth, a polymethyl metacrylate (PMMA) layer was spin-coated on top of the PtSe2.

These centimeter-scale PtSe2 thin films were transferred onto the substrate comprising 79 independent pressure devices, using a typical polymer supported transfer process as described for graphene.22 Each device consists of cavities covered by a patterned PtSe2 film located in between metal contacts (Figure 2a−c). The PMMA layer was not removed after the transfer in order to stabilize and protect the PtSe2 layer against environmental influences and to reduce possible cross sensitivity of the sensor. Details of the fabrication processes are described in the Methods section and in Figure S2a−d. A noninvasive Raman tomography cross-section, as demonstrated recently for graphene membranes,23 confirms the presence of free-standing PtSe2 across the cavity (Figure 2d,e) where devices with suspended PtSe2 (Figure 2e, top) and collapsed membrane (Figure 2e, bottom) were measured and can clearly be distinguished with this method. The corresponding spectrum of the suspended PtSe2 shows the characteristic Eg and A1g modes without the Si(I) peak (Figure 2d, top), whereas the spectrum taken at the bottom of the trench shows only the characteristic Si(I) peak of the Si substrate (Figure 2d, bottom). This clear separation is feasible due to the 1.4 μm deep cavity, which defines the distance between the suspended PtSe2 and the Si substrate.

The operation of the investigated pressure sensors can be described in the following way: the PtSe2/PMMA membranes seal the cavities and trap environmental pressure inside them.24−26 A different pressure (lower or higher) outside the

Figure 3. Comparison of all measured chips and devices as well as comparison of various pressure sensor devices using different materials for piezoresistive detection. (a) Box and whiskers plot of all measured chips, devices, and repeated measurements. (b) Comparison of the sensitivity in mbar−1 with other pressure sensors. (c) Comparison of the sensitivity normalized by membrane area in mbar−1 μm−2 with other pressure sensors. In plots (b) and (c), devices that require a separate membrane are indicated with a *, and the device with exceptionally high sensitivity is indicated by a black star.
cavity leads to a deflection of the PtSe₂ membrane. This deflection induces strain in the PtSe₂ layer, resulting in a change of its resistance. The chip design used in the present experiments includes devices of similar size without cavities as control references. The pressure sensors, after wire-bonding and packaging into a chip socket, were placed in a home-built pressure chamber where pressure can be regulated from 1000 mbar (environmental pressure) down to 200 mbar (Figure S3). The pressure, humidity, and temperature inside the chamber are recorded and controlled with commercial sensors during the experiments. Argon (Ar) atmosphere was used to exclude cross-sensitivity effects with gases and/or humidity. The current–voltage ($I–V$) characteristics of the PtSe₂ device for environmental pressure shows good linearity, i.e., the transferred PtSe₂ forms good Ohmic contacts with metal (gold) electrodes (Figure S4). The measured data is presented in Figure 2f along with the simultaneously measured pressure (dashed red line, right y-axis). The resistance across the PtSe₂ sensors decreases with applied increasing strain on the membrane (caused by the decrease in pressure, Figure S5a). A pressure difference of 800 mbar between the outside and the inside of the cavity leads roughly to 7% of change in resistance.

The results of four devices are displayed in Figure 2f: two intact membranes on cavities (filled green squares and filled blue triangles), one with a collapsed membrane (empty purple diamond) and one device without cavity for reference (empty black circles). A slight decrease (increase) in humidity during evacuation (venting) of the chamber is commonly observed for black circles. A slight decrease (increase) in humidity during the measurements.

A total of 19 working devices were measured on four different chips through 69 different measurements (Figure 3a). A sensitivity of $1.05 \times 10^{-4}$ mbar$^{-1}$ was extracted from Figure 2f. An average of $5.1 \times 10^{-4}$ mbar$^{-1}$ was calculated for all measured devices (best device not included). The results were compared to some other NEMS pressure sensors that operate in a similar pressure range (Figure 3b,c). These use gallium arsenide (GaAs),$^{27}$ Si nanowires (Si NWs),$^{15,16}$ single- and multiwalled carbon nanotubes (SWNT and MWNT)$^{14,17}$ and graphene$^{18,20}$ as the piezoresistive materials. However, for most of these (except Smith et al.$^{18}$ and Fung et al.$^{17}$), a separate membrane is needed, which is treated, or where the piezoresistive materials are grown or applied in a separate fabrication step. This adds additional complexity to the fabrication process, which is not the case for the PtSe₂-based pressure sensors because the material acts as membrane and sensor at the same time. The thickness of other material is limited due to their mechanical stability. The measured sensitivity outperforms the best reported 2D and low dimensional materials-based pressure sensors by a factor between 3 and 70 (Figure 3b). The SWNT-based pressure sensor$^{14}$ shows an equal sensitivity; however, the membrane areas are nearly 2 to 4 orders of magnitude larger than the PtSe₂ membrane. To take this into account the sensitivity can be normalized to the membrane area to receive a direct comparison between the devices independent of their membrane size.$^{28,18}$ Here, the PtSe₂-based pressure sensor shows nearly 2 to 5 orders of magnitude higher sensitivity than the other devices (Figure 3c; see also Table S6).

We further point out that one of the devices showed an exceptionally high sensitivity of $1.64 \times 10^{-3}$ mbar$^{-1}$ (Figure S5c). Even though it could not be reproduced in other devices, this value was repeatedly measured for that particular device (Figure 3a, device 2.1). The sensitivity and normalized sensitivity of this device are plotted in Figure 3b,c (black star). When normalized to the membrane area, this device is over 3 orders of magnitude more sensitive than the highest performing devices shown in Figure 3c (a SWNT$^{14}$ and a graphene membrane$^{18}$ based device), and 4 to 6 orders of magnitude more sensitive than other reported devices.

A bending beam setup was used to measure the piezoresistive gauge factor of the 4.5 and 9 nm thick PtSe₂ films, which

$$S = \frac{\Delta R}{R \Delta P}$$ (1)
consisted of 7 to 8 and approximately 15 layers, respectively. The bending beam setup enables measurements of well-defined strain fields in a very simple way (for details, see Supporting Information). The gauge factor (GF) can be extracted using eq 2:\(^2,2^9\)

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GF = \frac{\Delta R}{R_{if}}
\]  

Here, \(\epsilon\) is the strain in the bending beam at the position of the sensor (\(\epsilon = 0.04\%\)). A negative gauge factor (GF) of \(-84.8\) was obtained (Figure 4a; Supporting Information sections S7 and S9). The measured resistance change is shown in Figure 4b and Figure S9b for two PtSe\(_2\) layer thicknesses and masses of 2 and 0.5 kg (Figure S9c). A measurement of multiple strain cycles with a mass of 2 kg is shown in Figure S9d. In some measurements, the resistance did not immediately return completely to its initial values after removing the mass (Figure 4b, 4.5 nm PtSe\(_2\) device; Figure S9b,d). This may be attributed to a slip of the device or the electrical contacts during measurements due to nonoptimal adhesion to the beam. Furthermore, a slight overshoot followed by oscillations was observed for some devices right after applying the mass. These may be interpreted as natural oscillations due to the manual application of the mass on the beam. Data from a commercially available metal strain gauge is used as a reference (Figure 4b). A decrease in resistance with increasing strain on the PtSe\(_2\) film corroborates the integrated pressure sensor measurements (Figure S9a). The GF of the PtSe\(_2\) films exceeds the GF of the metal strain gauge (GF of 2)\(^2^9\) and of graphene (GF of 2–6).\(^2,2^4,3^0,3^1\) While similar or higher GF have been found for doped silicon (GF of −100 to +200)\(^2^9\) or mono- and trilayer MoS\(_2\) (GF of −148 and −43.5).\(^3^2\)

DFT calculations were conducted to gain insights into the observed resistance decrease with increased strain in PtSe\(_2\) films. The model was designed to represent the membrane covering the cavities of the PtSe\(_2\) pressure sensors. Here, the deformation can be thought of as biaxial strain acting on the lattice vectors and atomic positions. In the bulk system, biaxial strain means that the layers are stretched or compressed in plane. As bulk PtSe\(_2\) is metallic, the density of states (DOS) at the Fermi level is found to increase under biaxial tensile strain (\(\epsilon_a\)) and reduces under compression, as shown in Figure S10a. This result is in accordance with the experimental findings, where the resistivity decreases with increased \(\epsilon_a\).

Next, we have considered the effect of the interlayer strain and compression (\(\epsilon_c\)) on the DOS. The results are shown in Figure S10b. The compression of the interlayer distance has the opposite influence on the system, and it slightly reduces the DOS at the Fermi level. Finally, we have considered the two effects acting in tandem in the following way: for in-plane stretching, there is compression out of the plane, and vice versa (Figure S5a). The results for the combined effect are shown in Figure 5b. Once again, the DOS at the Fermi level is increased for the in-plane stretching and compression in the out-of-plane direction. However, the effect is reduced compared to just \(\epsilon_a\) due to the opposite effect of the interlayer compression, as shown in Figure S10b. In comparison to the significant increase of the DOS at the Fermi level upon strain, the band structure shows only minor changes (Figure S10c) not indicating strong differences in the effective masses under strain.

An increase in DOS has also been reported for other single and few layer semiconductor TMDs, like MoS\(_2\),\(^3^3\) MoSe\(_2\),\(^3^4\) WSe\(_2\),\(^3^4\) and also PtSe\(_2\).\(^3^5\) The semiconducting materials exhibit a decrease in band gap and even a transition to metallic behavior with applied strain, resulting in a negative gauge factor. For more detailed future studies, the influence of many other parameters should be considered and investigated, including the adhesive interface between the steel beam and the polyimide foil, the thickness and mechanical properties of the foil, and the PMMA layer covering the PtSe\(_2\). Also, the crystallographic orientations, thickness, and other material properties of the TAC-grown PtSe\(_2\) film need to be investigated and considered in the simulations. Nevertheless, the results of the simulations show a clear indication of an increase in DOS, leading to a decrease in resistance under the applied strain, which is the most plausible cause of the experimentally extracted negative GF.

We have demonstrated PtSe\(_2\)-based piezoresistive pressure sensors with high gauge factors and very high sensitivity. The experiments were conducted on large-area PtSe\(_2\) thin films grown by a scalable method of thermal conversion of metallic films at a low temperature of 400 °C. A negative gauge factor of approximately −85 was obtained from a PtSe\(_2\) strain gauge through bending beam experiments and can be understood in terms of a strain-induced increase in the DOS, as verified through DFT simulations. Furthermore, integrated piezoresistive pressure sensors were fabricated using PtSe\(_2\)/PMMA membranes. The PtSe\(_2\) pressure sensors showed very high sensitivity, outperforming piezoresistive pressure sensors based on other materials by at least a factor of 82. When normalized to the active membrane area, the sensitivity of our devices is almost 2 to 5 orders of magnitude larger than values reported for any other technology to date. One exceptional device has an even higher sensitivity of 1.64 × 10^3 mbar\(^{-1}\) and outperforms existing technologies by an even greater margin. These results suggest that layered 2D PtSe\(_2\) has great potential for future piezoresistive NEMS applications, beyond the demonstrated...
pressure sensors. These devices have a footprint that is up to 4 orders of magnitude smaller than other pressure sensors while showing a similar or even higher sensitivity. Further down-scaling to smaller cavities will improve the stability and yield of the membranes and allow decreasing the membrane thickness to maintain the high sensitivity. The low growth temperature and general complementary metal–oxide–semiconductor (CMOS) material compatibility makes PtSe2 highly attractive for future silicon technology integration.

**Methods.** Materials Synthesis and Analysis. Pt layers with a thickness of 1 and 2 nm were sputter-deposited on 1.5 × 1.5 cm² Si/SiO2 substrates using a Gatan coating system (Gatan 682 PECS) with a 19 mm diameter Pt target. A TAC process was used to selenize the predeposited Pt layers, as described in detail in refs 4 and 7. The cross-sectional Raman measurements were conducted using a WITec alpha 300R system with a 532 nm laser as the source of excitation. A laser power of 75 μW was used. For obtaining single Raman spectra, an 1800 g/mm grating was used, while the depth scan (cross-section) was conducted with a 300 g/mm grating. The system is limited to a lateral and vertical resolution of 300 and 900 nm, respectively.

Strain Gauge Fabrication. The strain gauges were fabricated by transferring as-grown PtSe2 films onto prepatterned polyimide foil substrates. A typical polymer-supported transfer method was used for the film transfer. PMMA (200 nm thick) (Allresist AR-P 649.04) was spun on the as-grown PtSe2 samples at a speed of 2000 rpm for 50 s. After spin-coating, the samples were annealed for 5 min at 80 °C to cure the PMMA. 2 M KOH was used to etch away the SiO2 layer and release the PMMA-covered PtSe2 films from the substrate. The PMMA-covered PtSe2 films were cleaned in DI-water, followed by a transfer to the prepatterned (500 nm thick copper contacts from evaporation) polyimide foil. After drying, the foil was glued (super glue Z70 by HBM) onto the steel beam (size of 200 mm × 1.5 mm × 0.3 mm, Figure S2c). The PtSe2 films grown from 1 nm initial Pt layers were transferred onto the device substrate using a PMMA-supported transport method as described above (Figure S2d). Lastly, the chip was wire bonded into a 44-pin PLCC chip package using 25 μm diameter Au wire.

Simulation. All calculations were performed using the DFT method as implemented in the VASP plane wave code.30,37 Ion–electron interactions were described by projector augmented wave approximation.38 We have employed the Perdew–Burke–Ernzerhof (PBE)39 functional under the generalized gradient approximation. van der Waals interaction corrections were included using the D3 approach proposed by Grimme.40 Cutoff energy was set to 600 eV, and the convergence threshold for residual force was 0.01 eV Å⁻¹. Brillouin zone integration was carried out at 6 × 6 × 6 Monkhorst–Pack k-grids. Spin–orbit coupling (SOC) was included in the electronic structure calculations. Bulk PtSe2 was fully optimized (lattice vectors and atomic positions) resulting in the following lattice vectors: a = b = 3.788 Å and c = 4.790 Å, and a distance between Se atoms in the Se–Pt–Se sandwich of 2.550 Å. This is in good agreement with the experimental data by Wang et al.,6 with a = b = 3.70 Å and the distance between Se atoms of 2.53 Å.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.8b00928.

Schematic of the growth of PtSe2 with additional Raman spectra. Fabrication process measurement chamber. I–V characteristics of the unstrained pressure device and additional electrical characterization data. Table of the compared pressure sensors from the literature. Strain gauge measurements, including the I–V characteristics of the device and further electrical measured data. Further DFT calculations for bulk and three-layer PtSe2 (PDF)

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Notes

The authors declare no competing financial interest.

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**ABBREVIATIONS**

2D, two-dimensional; PtSe2, platinum diselenide; TMD, transition metal dichalcogenides; MEMS, microelectromechanical systems; NEMS, nanoelectromechanical systems; DFT, density functional theory; TAC, thermally assisted conversion; Pt, platinum; GF, gauge factor; DOS, density of states; Si, silicon; SiO2, silicon oxide; AFM, atomic force microscopy; RMS, root-mean-square; PMMA, polymethyl metacrylate; Ar, argon; I–V, current–voltage; GaAs, gallium arsenide; Si NW,
REFERENCES


(2) Gupta, A.; Sathivel, T.; Seal, S. Recent Development in 2D Materials beyond Graphene. Prog. Mater. Sci. 2015, 73, 44.


