

PtSe₂ grown directly on polymer foil for use as a robust piezoresistive sensor

Article (Accepted Version)

Boland, Conor S, Ó Coileáin, Cormac, Wagner, Stefan, McManus, John B, Cullen, Conor P, Lemme, M C, Duesberg, Georg S and McEvoy, Niall (2019) PtSe₂ grown directly on polymer foil for use as a robust piezoresistive sensor. 2D Materials. ISSN 2053-1583

This version is available from Sussex Research Online: <http://sro.sussex.ac.uk/id/eprint/85221/>

This document is made available in accordance with publisher policies and may differ from the published version or from the version of record. If you wish to cite this item you are advised to consult the publisher's version. Please see the URL above for details on accessing the published version.

Copyright and reuse:

Sussex Research Online is a digital repository of the research output of the University.

Copyright and all moral rights to the version of the paper presented here belong to the individual author(s) and/or other copyright owners. To the extent reasonable and practicable, the material made available in SRO has been checked for eligibility before being made available.

Copies of full text items generally can be reproduced, displayed or performed and given to third parties in any format or medium for personal research or study, educational, or not-for-profit purposes without prior permission or charge, provided that the authors, title and full bibliographic details are credited, a hyperlink and/or URL is given for the original metadata page and the content is not changed in any way.

PtSe₂ grown directly on polymer foil for use as a robust piezoresistive sensor

Conor S. Boland, Cormac Ó Coileáin, Stefan Wagner, John B. McManus, Conor P. Cullen, Max C. Lemme, Georg S. Duesberg and Niall McEvoy**

Dr. C. S. Boland, School of Mathematical and Physical Sciences, University of Sussex, Sussex BN1 9QH, UK and School of Physics and AMBER, Trinity College Dublin, Dublin 2, Ireland
Email: c.s.boland@sussex.ac.uk

Dr. C. Ó Coileáin, J. B. McManus, C. P. Cullen, Dr. N. McEvoy, School of Chemistry and AMBER, Trinity College Dublin, Dublin 2 Ireland
Email: nmcevoy@tcd.ie

Dr. S. Wagner, Prof. M. C. Lemme, AMO GmbH, Advanced Microelectronic Center Aachen (AMICA), Otto-Blumenthal-Str. 25, 52074 Aachen, Germany

Prof. M. C. Lemme, Chair of Electronic Devices, Faculty of Electrical Engineering and Information Technology, RWTH Aachen University, Otto-Blumenthal-Str. 2, 52074 Aachen, Germany

Prof. G. S. Duesberg, Faculty of Electrical Engineering and Information Technology, EIT2 Universität der Bundeswehr München, 85577 Neubiberg, Germany

Keywords: PtSe₂, strain gauges, electromechanical sensors, piezoresistivity, flexible electronics, transition metal dichalcogenides

Robust strain gauges are fabricated by growing PtSe₂ layers directly on top of flexible polyimide foils. These PtSe₂ layers are grown by low-temperature, thermally-assisted conversion of predeposited Pt layers. Under applied flexure the PtSe₂ layers show a decrease in electrical resistance signifying a negative gauge factor. The influence of the growth temperature and film thickness on the electromechanical properties of the PtSe₂ layers is investigated. The best-performing strain gauges fabricated have a superior gauge factor to that of commercial metal-based strain gauges. Notably, the strain gauges offer good cyclability and are very robust, surviving repeated peel tests and immersion in water. Furthermore, preliminary results indicate that the stain gauges also show potential for high-

1
2
3 frequency operation. This host of advantageous properties, combined with the possibility of
4 further optimization and channel patterning, indicate that PtSe₂ grown directly on polyimide
5 holds great promise for future applications.
6
7
8
9

10 11 12 **Introduction**

13
14 The emergence of 2D materials has triggered a proliferation of new research topics with
15 much focus placed on synthesizing and modifying these materials for use in a wide array of
16 potential applications. Many members of the transition metal dichalcogenide (TMD) family
17 possess a bandgap and so have been touted for use in applications ranging from transistors,
18 to photodetectors, to sensors.¹ Most studies to date have focused on semiconducting
19 group-6 TMDs, such as MoS₂ or WSe₂, which occur naturally in the 2H phase. However,
20 recent reports have outlined the practicality of growing noble-metal, or group-10, TMDs
21 such as PtSe₂, which occurs naturally in the 1T phase. Interestingly, the band structure of
22 PtSe₂ is heavily dependent on its layer thickness with bulk films having semimetallic
23 character while mono- and few-layer films are semiconducting.²⁻⁴
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39

40 Vapour-phase growth methods, such as chemical vapour deposition (CVD) and thermally
41 assisted conversion (TAC), offer scalable growth of TMD layers with reasonable to good
42 crystalline quality.⁵⁻⁶ While MoS₂ and related materials synthesized in this manner have
43 shown impressive performance, their practical use has been somewhat hampered by the
44 associated high growth temperature (typically > 600°C). This high temperature restricts the
45 choice of substrate and renders the growth process incompatible with standard
46 semiconductor processes, such as back-end-of-line (BEOL) processing. On the other hand,
47 PtSe₂ can be grown at a relatively low growth temperature by a TAC process.⁷⁻⁸ The material
48 grown in this manner is nanocrystalline but, despite this, studies have indicated that it holds
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 promise for applications in photodetectors,⁹⁻¹⁰ gas sensing,⁸ electronics¹¹⁻¹³ and
4
5 electrocatalysis.¹⁴ This relatively low growth temperature means that PtSe₂ can be grown
6
7 directly on substrates that are inaccessible to standard vapour-phase growth processes for
8
9 TMDs.
10
11

12
13 Strain gauges, simple sensors that undergo a change in electrical resistance under applied
14
15 strain, have broad applications in areas such as health monitoring,¹⁵ civil engineering and
16
17 construction¹⁶ and semiconductor microsystems.¹⁷ Recently, there has been an emergent
18
19 need for robust, sensitive and low-power strain gauges in civil engineering that can be applied
20
21 to monitor stresses on wind turbine blades¹⁸ and bases¹⁹ in extreme conditions. Through
22
23 better understanding of the forces applied, the construction of more-efficient, green-energy
24
25 generating structures is made possible. Such strain gauges are generally based on materials
26
27 that exhibit piezoresistive properties. Upon the application of strain, ε , electrical resistance
28
29 changes such that
30
31
32
33
34

$$\Delta R / R_0 = G\varepsilon$$

$$G = \frac{1}{\rho_0} \frac{d\rho}{d\varepsilon} + (1 + 2\nu)$$

35
36
37
38
39
40
41
42
43
44
45 Where G is the sensitivity metric known as the gauge factor measured at low strain, ρ_0 is the
46
47 material's zero-strain resistivity, ρ is the resistivity and ν is the Poisson ratio.²⁰
48
49

50
51 Most commercially-available sensors are metal-based foils on a rigid polymer backing that
52
53 tend to have low values of G in the range of 2-4.²⁰ This is due to metals undergoing small
54
55 changes in resistivity with applied strain. However, for many semiconducting materials
56
57 applying strain leads to changes in the band structure which can modify either carrier density
58
59
60

1
2
3 or mobility, resulting in large changes in resistivity and thus high values of G. For p-type silicon,
4
5 G values up to ~175 have been reported.¹⁷ However, such materials are often brittle resulting
6
7 in small sensing ranges, i.e. failure occurs at low strain. Much research has also focused on
8
9 the use of networks of nanomaterials, such as carbon nanotubes,²¹⁻²² nanowires²³ and metal
10
11 nanoparticles,²⁴ as a conductive filler in a polymer matrix to produce composites with strain-
12
13 dependent electrical properties. While such composites often possess large gauge factors
14
15 they typically display poor environmental stability and need to be encapsulated.
16
17
18

19
20
21 Research has turned towards materials science, and more specifically 2D materials, in an
22
23 effort to overcome these challenges. Many 2D materials display piezoresistive properties
24
25 suggesting they could find use as active components in assorted electromechanical sensors
26
27 such as strain gauges, as well as MEMS and NEMS devices.²⁵⁻²⁷ Individual flakes of MoS₂, a
28
29 semiconducting 2D material, have been shown to have negative gauge factors ranging from
30
31 -225 for bilayers to -50 for few-layer samples.²⁶ Most recently, pressure sensors and strain
32
33 gauges based on TAC-grown PtSe₂, which was grown on SiO₂/Si and subsequently
34
35 transferred onto flexible substrates, have been demonstrated.²⁸ The fabrication process for
36
37 such devices could be greatly simplified by direct growth of PtSe₂ on flexible substrates.
38
39 Additionally, without the need for polymer-based transfer processes, cleaner interfaces and
40
41 resultant improved device performance can be anticipated. Furthermore, TAC growth is
42
43 compatible with standard processing and patterning techniques and so different device
44
45 geometries could be patterned directly on flexible substrates.
46
47
48
49
50
51

52
53 Herein we demonstrate the growth of PtSe₂ layers directly on flexible polyimide foils. These
54
55 films adhere strongly to the polyimide substrate and are continuous and conductive over
56
57 large areas. The flexibility of polyimide means that the effect of flexure, and other strain, on
58
59
60

1
2
3 the PtSe₂ layers can be investigated. The PtSe₂ layers show a strong and stable electrical
4
5 response to flexure suggesting that they could be used in future electromechanical sensors.
6
7
8
9

10 11 **Results and Discussion**

12 PtSe₂ thin films were grown on polyimide substrates by a TAC process as depicted in **Figure**
13
14 **1(a)** and described in more detail in our previous reports.⁷⁻⁸ Substrates were typically ~2 cm
15
16 x 4 cm in area, as shown in **Figure 1(b)**, but larger or smaller substrates could readily be
17
18 made. Scanning electron microscopy (SEM) and scanning probe microscopy were used to
19
20 examine the topography and uniformity of the films grown. A SEM image of a PtSe₂ film
21
22 derived from 1 nm Pt on polyimide, converted to PtSe₂ at 400 °C, is shown in **Figure 1(c)**.
23
24 This image shows film continuity over a large area and also highlights the nanocrystalline
25
26 morphology, which is typical for TAC-grown TMD films.¹³ Additional SEM images at lower
27
28 magnification are shown in Figure S1(a) of the Supporting Information and indicate that the
29
30 PtSe₂ conforms to features on the polyimide surface. Atomic force microscopy (AFM) was
31
32 also used to investigate the morphology of PtSe₂ on polyimide, prepared under the same
33
34 conditions, as shown in **Figure 1(d)**. Like the SEM image, the AFM image shows the
35
36 nanocrystalline nature of the PtSe₂. A root-mean-square (RMS) roughness of 4.6 nm was
37
38 extracted for PtSe₂ films grown from 1 nm Pt on polyimide, which is comparable with TAC-
39
40 derived PtSe₂ films grown on other substrates, such as SiO₂/Si. Conductive-AFM (or c-AFM)
41
42 imaging was also performed on the PtSe₂ films as shown in **Figure 1(e)**. This image was
43
44 taken over a large area (30 x 30 μm) and highlights the uniformity in the conductivity of the
45
46 film at this scale. The chemical composition of the films grown was probed by X-ray
47
48 photoelectron spectroscopy (XPS). The Pt 4f and Se 3d spectral regions for a 1 nm Pt film
49
50 converted at 400 °C are shown in **Figure 1(f)**. These spectra are consistent with previous
51
52
53
54
55
56
57
58
59
60

reports for PtSe₂ grown on more conventional Si-based substrates and indicate that stoichiometric PtSe₂ is formed by our process.⁸ The Pt 4f PtSe₂ component was found to be at a binding energy of ~73 eV, a minor component likely from platinum oxide was also present at ~72 eV. For the Se 3d core level spectral region the PtSe₂ main component was present at ~54.5 eV. A much lower concentration component at ~55.5 eV was attributed to the presence of edge/amorphous Se in the sample. Raman spectroscopy is usually one of the first tools used to confirm the presence of PtSe₂ or other TMDs⁷ but in the case of direct growth on polyimide it is not possible to get a strong signal.

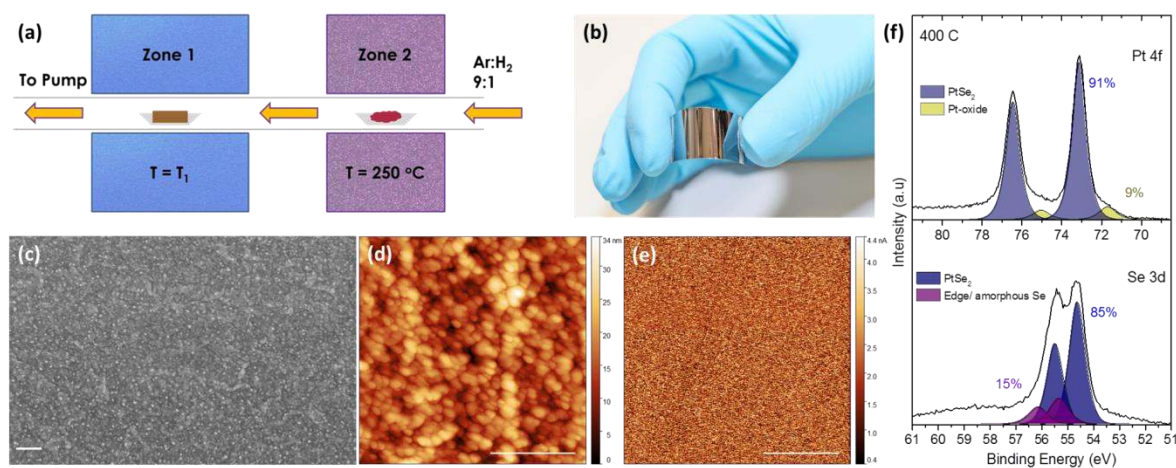


Figure 1 (a) Schematic of TAC process in two-zone furnace. Analysis of PtSe₂ film grown from 1 nm thick Pt on polyimide at a conversion temperature of 400 °C (b) Photograph of PtSe₂ film grown directly on polyimide foil. (c) SEM image of PtSe₂ film on polyimide, scale bar is 200 nm. (d) AFM image of PtSe₂ film on polyimide, scale bar is 500 nm. (e) c-AFM image of PtSe₂ film on polyimide showing uniform conductivity over the relatively large area probed, scale bar is 10 μm. (f) Pt 4f and Se 3d core level XPS spectra of PtSe₂ film on polyimide.

The electromechanical properties of PtSe₂ on polyimide were tested by flexing the films while simultaneously measuring the films' resistance using a custom-made, three-point flexure rig, as detailed in the methods section. Under applied strain a decrease in resistance was observed, resulting in a negative gauge factor consistent with previous reports on other

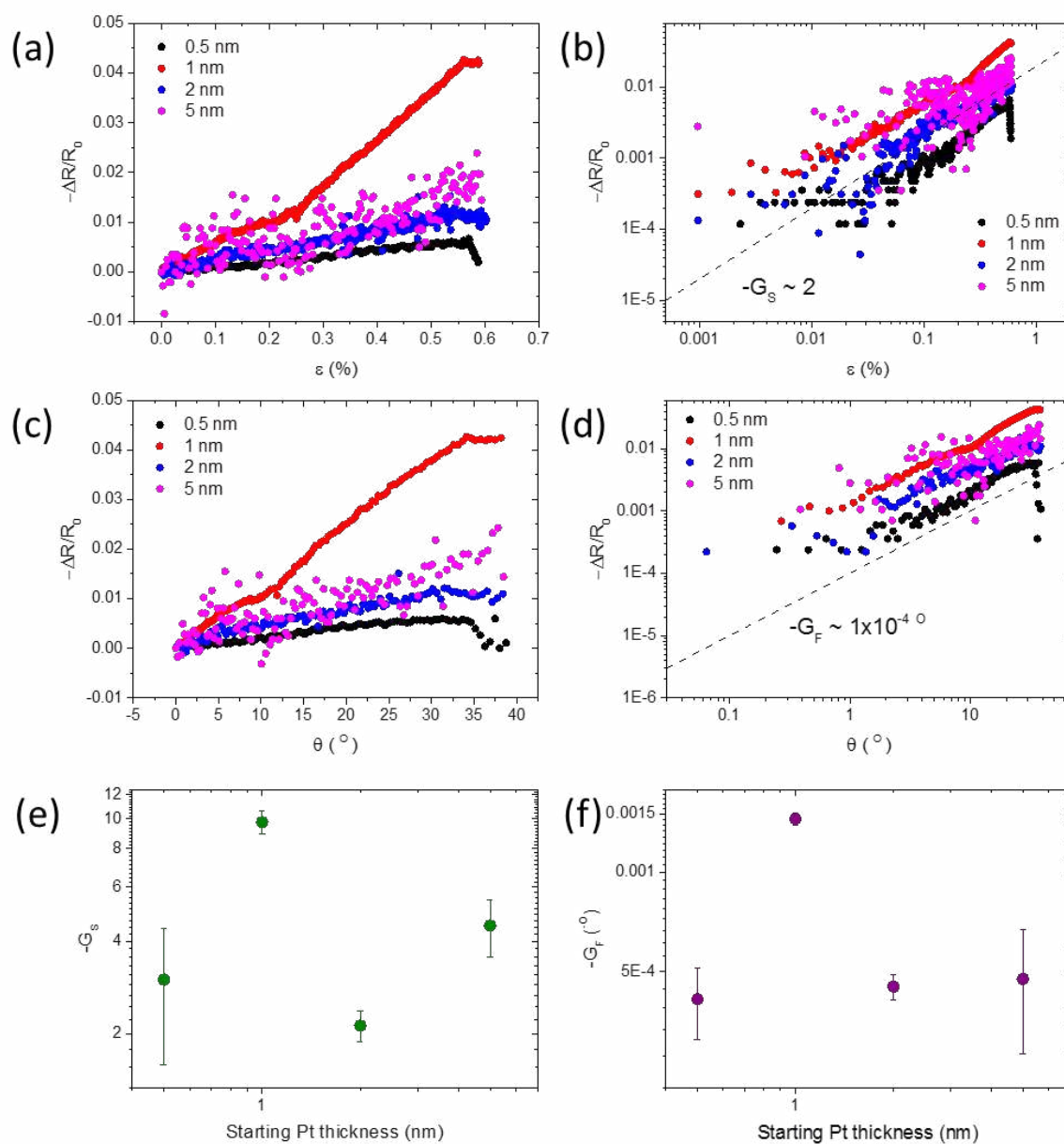
1
2
3 TMDs²⁶, and also with previous experimental reports on PtSe₂ films transferred onto a
4
5 bending-beam cantilever setup.²⁸ In previous reports on TMDs, the negative gauge factor
6
7 has been attributed to an increase in the density of states (DOS) and a decrease in the size
8
9 of the bandgap under applied strain.^{26, 28} The effect of film thickness on the
10
11 electromechanical properties was examined by converting Pt films of different starting
12
13 thicknesses to PtSe₂ at 400 °C. Like other TMDs, the band structure and electronic
14
15 properties of PtSe₂ depend on layer thickness; it is semiconducting in its mono- and few-
16
17 layer form it is semimetallic in its bulk form.^{3, 7} Plots of fractional resistance change versus
18
19 applied strain, for different film thicknesses, are shown as a function of applied strain
20
21 **(Figure 2(a, b))** and flexure angle **(Figure 2(c, d))**. The labelled thicknesses on the plots refer
22
23 to the starting Pt film thickness (i.e. the film thickness before TAC). It is clear from these
24
25 data that the films from 1 nm starting thickness of Pt have the best properties in terms of
26
27 electromechanical response and signal-to-noise ratio. This is supported by the extracted
28
29 gauge factors, shown in **Figure 2(e, f)**, which are highest for the 1 nm film. The associated
30
31 strain-related gauge factor is 12, which is superior to that of typical commercial metal-based
32
33 strain gauges. This value is considerably lower than that reported for MoS₂ by Manzeli *et*
34
35 *al.*²⁶ However, it is important to note that their experiments entailed measuring the
36
37 response of an individual, suspended flake, with lateral dimensions on the order of microns,
38
39 which was deformed using an AFM cantilever whereas we are looking at large-area films,
40
41 consisting of nanocrystalline domains, grown directly on a polymer substrate. A closer point
42
43 of comparison for our results is recently-reported work on MoS₂/polymer composites which
44
45 display similar gauge factors to our films.²⁹ It is likely that the electromechanical
46
47 performance of our films could be improved through patterning of the channel i.e. a
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 serpentine channel, similar to those used in commercial strain gauges, could be defined by
4
5 optical lithography.
6
7

8 Our previous studies indicated that conversion of 1 nm of Pt resulted in PtSe₂ films with a
9
10 thickness of ~3.5 nm (or ~5 layers).¹³ At this layer thickness it is possible that the films are
11
12 still partially semiconducting in character as there is some debate in the literature as to the
13
14 exact layer thickness at which PtSe₂ transitions from semiconducting to semimetallic.^{2, 30-31}
15
16

17 One would perhaps expect a film of 0.5 nm Pt starting thickness to be more sensitive as the
18
19 resultant PtSe₂ would be more semiconducting in nature.¹³ However, the film uniformity
20
21 and conductivity must also be considered. Films grown from 1 nm Pt were also tested in a
22
23 cantilever bending-beam setup and showed comparable results to previously-investigated
24
25 transferred PtSe₂ films as detailed in the Supporting Information, S2. It is interesting that all
26
27 films display a negative gauge factor given that the thicker films are expected to be
28
29 semimetallic. This is consistent with previous results on transferred PtSe₂ films where
30
31 density functional theory calculations were used to explain the negative gauge factor in the
32
33 high-strain regime.²⁸ These calculations indicated an increase in the DOS at the Fermi level
34
35 under applied tensile strain which was offset slightly by a decrease in the DOS at the Fermi
36
37 level due to the associated interlayer compression. Previous experimental reports have
38
39 shown negative gauge factors for MoS₂²⁶ and positive gauge factors for graphene.³²
40
41 Whereas theoretical investigations have suggested that MoSe₂ and WSe₂ have positive
42
43 gauge factors.³³ It is clear that more detailed investigation will be required to fully
44
45 understand the sign of the gauge factor for PtSe₂ and other 2D materials. This is particularly
46
47 complicated in the case of TAC-grown PtSe₂ where the layer thickness has a massive impact
48
49 on the electrical properties and the nano-sized crystalline domains are very different to the
50
51 idealized highly-crystalline scenario. Reference films of Pt only, with no selenisation
52
53
54
55
56
57
58
59
60

1
2
3 treatment, show a smaller positive gauge factor when subjected to the same
4
5
6 electromechanical tests, as detailed in the Supporting Information, Figure S3. This is the
7
8 expected behavior for metallic films. Interestingly, films which are sulfurised rather than
9
10 selenised also show a positive gauge factor, as shown in Figure S4 of the Supporting
11
12 Information. In this case it is probable that PtS rather than PtS₂ is formed under the low-
13
14 pressure conversion conditions used, in line with previous reports.¹³
15
16
17
18



1
2
3 *Figure 2 Investigation of the effect of PtSe₂ film thickness on the electromechanical response (a, b) Fractional*
4 *resistance change as a function of applied strain. (c, d) Fractional resistance change as a function of flexure*
5 *angle. (e, f) Extracted gauge factors for films of different thickness.*
6
7
8
9

10
11 Our previous studies indicated that a temperature of ~400 °C is required for complete
12 conversion of Pt to PtSe₂. However, other reports have shown that PtSe₂ can be grown by
13 epitaxial means on single-crystal Pt at temperatures as low as 270 °C.³ With this in mind, we
14 examined the electromechanical properties of PtSe₂ films formed by converting 1 nm Pt at
15 different temperatures. Shown in **Figure 3(a)** is the fractional resistance change versus
16 strain for films converted at temperatures in the range 250-450 °C. It is worth noting that
17 the polyimide substrate would not survive temperatures higher than this and, furthermore,
18 PtSe₂ would not form. **Figure 3(a)** indicates that the strongest electromechanical response is
19 obtained from films with a conversion temperature of 400 °C. These films have the lowest
20 resistance and highest (negative) gauge factor as shown in **Figure 3(b)** and **3(c)**, respectively.
21 This suggests that complete conversion of Pt to PtSe₂ is required for a strong
22 electromechanical response – although it is also possible that the crystallinity, and in turn
23 the electrical properties, of the films depends on the conversion temperature as seen
24 previously for TAC-grown MoS₂ films.⁵ XPS data for the films converted at different
25 temperatures are shown in the Supporting Information, Figure S5. These suggest a greater
26 contribution from Pt oxides and amorphous Se at the lowest growth temperature used.
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

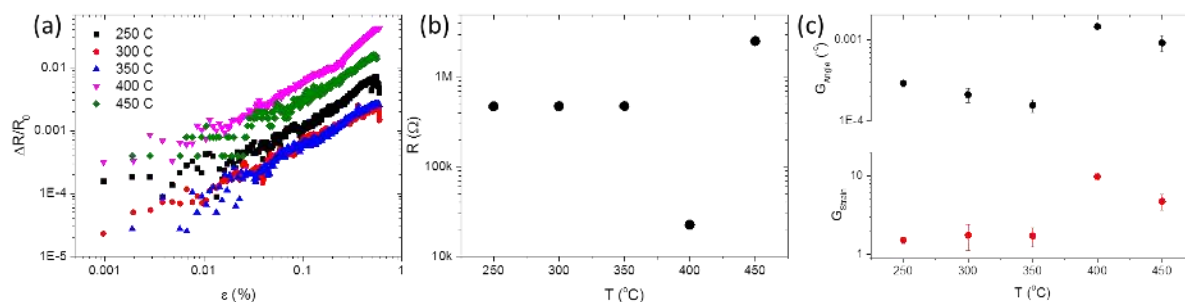


Figure 3(a) Fractional resistance change as a function of applied strain for 1 nm Pt films on polyimide which were converted to PtSe₂ at different temperatures. (b) Measured resistance values for PtSe₂ films grown at different temperatures. (c) Extracted gauge factor for PtSe₂ films grown from 1 nm Pt at different temperatures.

The results of cycled testing on a 1 nm Pt film on polyimide, which was converted to PtSe₂ at 400 °C, are shown in **Figure 4(a)**. It is clear from this that the electromechanical response is stable over many cycles. Data acquired over a longer timeframe are shown in the Supporting Information, Figure S6. The effect of repeated peeling of the active PtSe₂ layer on a PtSe₂/polyimide sample (grown from 1 nm Pt) with sticky tape is shown in **Figure 4(b)**. While an increase in the film resistance is observed, this peeling does not have a drastic effect on the electrical properties of the channel suggesting that the PtSe₂ adheres very strongly to the polyimide substrate and that the sensors possess good mechanical stability. This strong adhesion to polyimide is noteworthy as structural robustness is paramount if any real-world sensing applications are to be considered. The strong adhesion is also interesting when one considers that previous studies have indicated that PtSe₂ can be easily transferred off SiO₂/Si substrates.⁸ This indicates that the choice of growth substrate has a big influence on the strength of the PtSe₂/substrate interaction. The effect of soaking PtSe₂/polyimide (grown from 1 nm Pt) in water and acetone for a period of 5 days is shown in **Figure 4(c, d)**. Immersion in water has a minimal effect on the electromechanical properties suggesting

that strain gauges based on PtSe₂/polyimide possess good environmental stability and could be used in aqueous conditions. Immersion in acetone on the other hand has a severe impact on the electromechanical properties. As polyimide is known to be resistant to acetone the reason for this performance degradation is unclear. A detailed study of the effect of different chemical environments on the properties of PtSe₂/polyimide would help to explain this behaviour and should form the basis of future work in this area. Additional detail on these solvent soak tests is presented in the Supporting Information, Figure S7 and S8. Overall, the PtSe₂/polyimide strain gauges produced offer good cyclability and stability. These properties are worth highlighting as strain gauges based on nanomaterial/polymer composites typically suffer from poor environmental stability unless they are encapsulated.

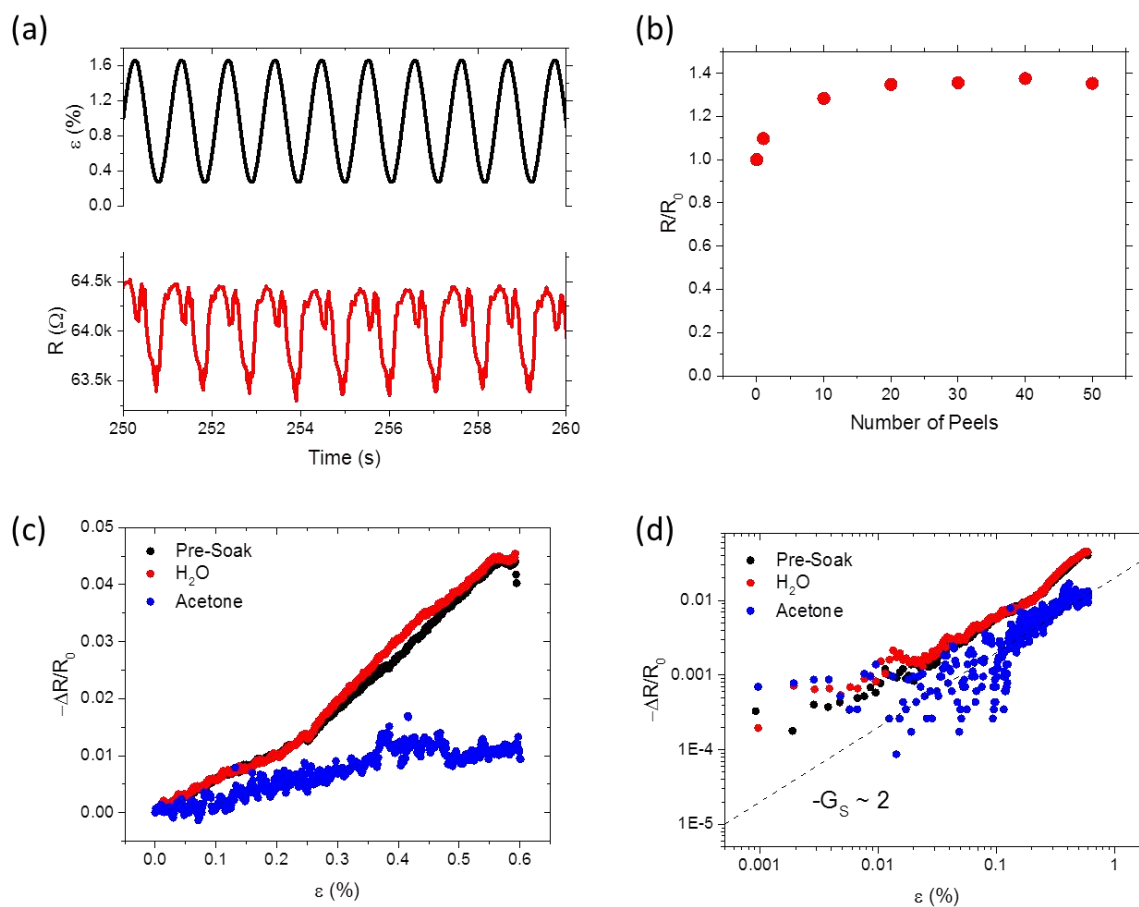


Figure 4(a) Cycled electromechanical response of PtSe₂ on polyimide (from 1 nm Pt). The black line shows the applied strain and the red line shows the change in resistance (b) Fractional resistance change of PtSe₂ on

polyimide upon repeated peeling. While there is an increase in the resistance the film is still conductive following 50 peels (c, d) Fractional resistance change of reference PtSe_2 on polyimide, and films that have been immersed in solvent (water or acetone) for 5 days, under applied strain.

Preliminary tests were carried out to investigate the response of piezoresistive sensors based on PtSe_2 on polyimide to vibrations of different frequencies. This was achieved by attaching a film to a speaker that was then operated at different frequencies. The results of this are shown in Figure 5(a) where a strong signal, with a high signal-to-noise ratio, is seen for vibrations with frequencies of 95 Hz, 190 Hz and 380 Hz. This is further emphasized by the zoomed-in view of the response to vibrations of 380 Hz shown in Figure 5(b). This strong response to high-frequency mechanical vibrations suggests that these sensors could potentially be used to monitor the performance of machinery or other structures with moving/vibrating parts.

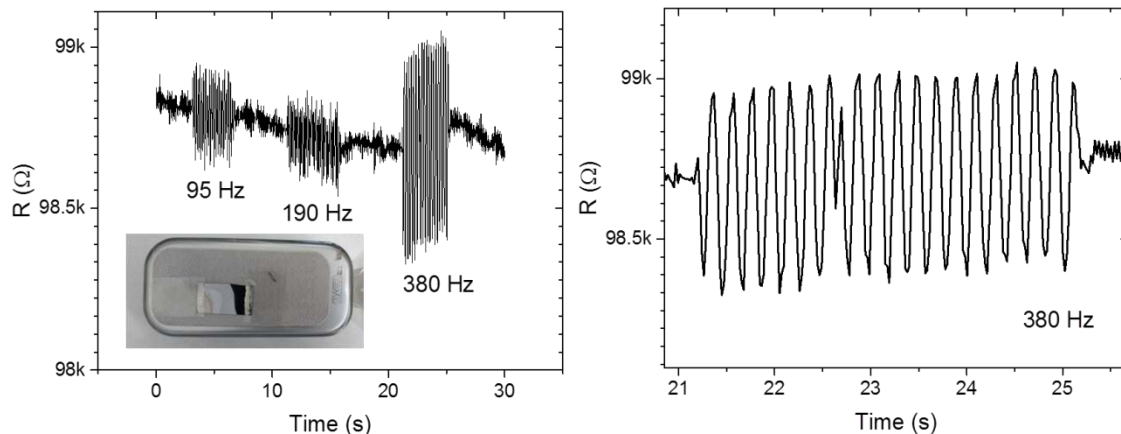


Figure 5(a) Resistance change of PtSe_2 /Polyimide attached to a speaker which is operated at different frequencies. Inset: photograph of PtSe_2 /Polyimide attached to speaker (b) Zoomed-in view of change in resistance of PtSe_2 /Polyimide when speaker is operated at 380 Hz.

Conclusion

1
2
3 Thin films of PtSe₂ have been grown directly on flexible polyimide foil and subsequently
4 assessed for use as strain gauges. These films show superior gauge factors compared to
5 commercial metal-based strain gauges. We have investigated the effect of growth
6 temperature and film thickness on the performance of PtSe₂/polyimide strain gauges. The
7 strain gauges were shown to be robust and stable over many cycles. The PtSe₂ layer adheres
8 very strongly to the polyimide, with the films remaining conductive after repeated peel
9 tests. The strain gauges show no sign of degradation following immersion in water for
10 prolonged periods. A preliminary investigation showed that the strain gauges are well-suited
11 to high-frequency operation. The combination of sensitivity, stability and robustness means
12 that these strain gauges could potentially be used to monitor repeated vibrations, possibly
13 in an outdoor setting. Lastly, strain gauges are but a very simple example of a technology
14 based on PtSe₂ grown on a flexible substrate. We envisage that similar approaches could be
15 developed to fabricate other, more complicated components for flexible electronics.

35 **4. Experimental Section**

36 *PtSe₂ Growth:* PtSe₂ layers were grown by a TAC process as detailed elsewhere previously.⁷⁻⁸
37 Pieces of polyimide foil of 125 μm thickness (Upilex 125S, UBE Europe GmbH) were used as
38 substrates. Pt layers of different thickness were deposited on top of the substrates by e-
39 beam evaporation (Temescal FC-2000). These Pt layers were then converted to PtSe₂ in a
40 custom-designed, two-zone furnace whereby the Pt/polyimide was heated to a set-point
41 temperature in zone 1 and Se powder was heated to 250 °C in the upstream zone 2 of the
42 furnace. Forming gas (90% Ar, 10% H₂) flow at 150 sccm carried Se vapour from zone 2 to
43 zone 1 of the system. A dwell time of 2 hours was used, previously shown to be sufficient for
44 complete conversion of Pt to PtSe₂.

1
2
3 *Characterization:* Atomic force microscopy was performed using a Bruker multimode 8
4
5 system. The topographical and conductive mappings were acquired by PeakForce (PF)
6
7 tapping using the PF-TUNA mode, with standard PF-TUNA probes. The DC bias ranged from
8
9 25-100 μV , and the contact current is displayed (the averaged current during the contacted
10
11 portion of the force curve.)
12
13

14
15 The XPS data were collected using an Omicron XM1000 MkII X-ray source with
16
17 monochromatic Al $K\alpha$ X-rays alongside an Omicron EA125 energy analyzer. An analyzer pass
18
19 energy of 15 eV was used for the collection of all core-level spectra. An Omicron CN10
20
21 electron flood gun was used for charge compensation and the binding energy scale was
22
23 referenced to the carbon 1s core level at 284.8 eV. Analysis and fitting of the spectral
24
25 components was performed using CasaXPS software. Spectral components were fitted using
26
27 a Shirley background subtraction and Gaussian-Lorentzian line shapes.
28
29

30
31 Scanning electron microscopy imaging was done using a Zeiss Ultra Plus SEM operating at
32
33 3 kV with an in-lens detector.
34
35

36
37 *Electromechanical Characterisation:* Electromechanical measurements during flexure tests
38
39 were performed using a Keithley KE2601 source meter in 2-probe mode, controlled by
40
41 LabView software, in conjunction with a Zwick Z0.5 ProLine Mechanical Tester (100 N Load
42
43 Cell). For electromechanical flexure tests, sample specimens were hand-cut with a blade
44
45 into 20 mm x 17.5mm (L x W) dimensions. Silver wire contacts were painted directly onto
46
47 the grown PtSe₂ layer at each end of the sample and attached to the source meter via
48
49 crocodile clips.
50
51
52

53
54
55 For the flexure testing, a custom made three-point flexure rig was used. Samples were
56
57 placed with the PtSe₂ side lying face down across two insulating support pins. The mechanical
58
59
60

1
2
3 tester driven loading pin was then lowered into its start position ($\epsilon = 0$) resting against the
4
5 upward facing substrate side. Samples were then strained at a rate of 10 mm/min until $\epsilon \sim$
6
7
8 0.8%.
9

10
11 Bending-beam experiments were conducted by attaching hand-cut samples with super glue
12
13 (super glue Z70 by HBM) to a steel beam (300 mm long, 30 mm wide and 3 mm thick) at a
14
15 location 200 mm from the free-standing end of the beam. Masses of 2 kg and 1 kg were
16
17 attached to the end of the beam resulting in a strain of 0.04 % and 0.02%, respectively. The
18
19 resistance across the PtSe₂ was measured with a Keithley 4200 SCS parameter analyser with
20
21 0.1 ms pulses at ± 3 V, ± 5 V and ± 7 V. Measurements were also conducted for tensile
22
23 (sample at the top of the beam) and compressive (sample at the bottom of the beam) strain.
24
25
26
27
28

29 *Durability Testing:* For all testing, a new PtSe₂ layer grown from 1 nm Pt on a 125 μ m thick
30
31 polyimide substrate was used for each test. This sample type was chosen due to its high
32
33 electromechanical response. For cyclic testing, contacts were painted on the sample. The
34
35 sample was then placed in the three-point flexure rig and deformed under a sine wave
36
37 strain output at a frequency of 1 Hz between $\epsilon \sim 0.2\%$ and $\sim 1.2\%$ for 500 cycles while
38
39 measuring the electrical response as a function of time. For the tape peel test, clear
40
41 domestic scotch tape was rubbed on the PtSe₂ layer of the sample and peeled off, by hand,
42
43 50 times. After each peel, the piece of tape was replaced with a new one to maintain a
44
45 constant adhesion. The electrical properties of the sample were measured at the 0th, 1st,
46
47 10th, 20th, 30th, 40th, and 50th peel using a multimeter. For the solvent soak test, three
48
49 separate samples (one for reference) were soaked in normal tap water and acetone. Every
50
51 24 hrs, up to 120 hrs, samples were removed from their respective liquid and oven dried at
52
53
54
55
56
57
58
59 50° C for 10 mins. Electrical properties were then measured using a multimeter, after which,
60

1
2
3 the samples were returned to their soak. After the 120 hrs had elapsed, flexure tests were
4
5 performed on the three samples.
6
7

8 9 **Supporting Information**

10 Supporting Information is available online
11
12
13

14 15 **Acknowledgements**

16
17
18 N. Mc E. acknowledges support from Science Foundation Ireland (SFI) through
19
20 15/SIRG/3329. G. S. D., C. Ó C. and C. P. C. acknowledge the support of SFI under Contract
21
22 No. 12/RC/2278 and PI15/IA/3131. J. B. Mc M. acknowledges an IRC scholarship under
23
24 Award 13653. G. S. D and M. C. L. acknowledge the Graphene Flagship under Contract
25
26 785219. We thank UBE Europe GmbH for providing polyimide foils.
27
28
29
30

31 32 **References**

- 33
34 1. Choi, W.; Choudhary, N.; Han, G. H.; Park, J.; Akinwande, D.; Lee, Y. H., Recent
35 development of two-dimensional transition metal dichalcogenides and their applications.
36 *Materials Today* **2017**, *20* (3), 116-130.
- 37 2. Ciarrocchi, A.; Avsar, A.; Ovchinnikov, D.; Kis, A., Thickness-modulated metal-to-
38 semiconductor transformation in a transition metal dichalcogenide. *Nature Communications*
39 **2018**, *9* (1), 919.
- 40 3. Wang, Y.; Li, L.; Yao, W.; Song, S.; Sun, J. T.; Pan, J.; Ren, X.; Li, C.; Okunishi, E.;
41 Wang, Y.-Q.; Wang, E.; Shao, Y.; Zhang, Y. Y.; Yang, H.-t.; Schwier, E. F.; Iwasawa, H.;
42 Shimada, K.; Taniguchi, M.; Cheng, Z.; Zhou, S.; Du, S.; Pennycook, S. J.; Pantelides, S. T.;
43 Gao, H.-J., Monolayer PtSe₂, a New Semiconducting Transition-Metal-Dichalcogenide,
44 Epitaxially Grown by Direct Selenization of Pt. *Nano Letters* **2015**, *15* (6), 4013-4018.
- 45 4. Yan, M.; Wang, E.; Zhou, X.; Zhang, G.; Zhang, H.; Zhang, K.; Yao, W.; Lu, N.;
46 Yang, S.; Wu, S.; Yoshikawa, T.; Miyamoto, K.; Okuda, T.; Wu, Y.; Yu, P.; Duan, W.;
47 Zhou, S., High quality atomically thin PtSe₂ films grown by molecular beam epitaxy. *2D*
48 *Materials* **2017**, *4* (4), 045015.
- 49 5. Gatensby, R.; Hallam, T.; Lee, K.; McEvoy, N.; Duesberg, G. S., Investigations of
50 vapour-phase deposited transition metal dichalcogenide films for future electronic
51 applications. *Solid-State Electronics* **2016**, *125*, 39-51.
- 52 6. Kim, S.-Y.; Kwak, J.; Ciobanu, C. V.; Kwon, S.-Y., Recent Developments in
53 Controlled Vapor-Phase Growth of 2D Group 6 Transition Metal Dichalcogenides. *Advanced*
54 *Materials* *0* (0), 1804939.
- 55 7. O'Brien, M.; McEvoy, N.; Motta, C.; Zheng, J.-Y.; Berner, N. C.; Kotakoski, J.;
56 Elibol, K.; Pennycook, T. J.; Meyer, J. C.; Yim, C.; Abid, M.; Hallam, T.; Donegan, J. F.;
57
58
59
60

- 1
2
3 Sanvito, S.; Duesberg, G. S., Raman characterization of platinum diselenide thin films. *2D*
4 *Materials* **2016**, *3* (2), 021004.
- 5
6 8. Yim, C.; Lee, K.; McEvoy, N.; O'Brien, M.; Riazimehr, S.; Berner, N. C.; Cullen, C.
7 P.; Kotakoski, J.; Meyer, J. C.; Lemme, M. C.; Duesberg, G. S., High-Performance Hybrid
8 Electronic Devices from Layered PtSe₂ Films Grown at Low Temperature. *ACS Nano* **2016**,
9 *10* (10), 9550-9558.
- 10
11 9. Yim, C.; McEvoy, N.; Riazimehr, S.; Schneider, D. S.; Gity, F.; Monaghan, S.;
12 Hurley, P. K.; Lemme, M. C.; Duesberg, G. S., Wide Spectral Photoresponse of Layered
13 Platinum Diselenide-Based Photodiodes. *Nano Letters* **2018**, *18* (3), 1794-1800.
- 14
15 10. Zeng, L.; Lin, S.; Lou, Z.; Yuan, H.; Long, H.; Li, Y.; Lu, W.; Lau, S. P.; Wu, D.;
16 Tsang, Y. H., Ultrafast and sensitive photodetector based on a PtSe₂/silicon nanowire array
17 heterojunction with a multiband spectral response from 200 to 1550 nm. *NPG Asia Materials*
18 **2018**, *10* (4), 352-362.
- 19
20 11. Li, L.; Xiong, K.; Marsell, R. J.; Madjar, A.; Strandwitz, N. C.; Hwang, J. C. M.;
21 McEvoy, N.; McManus, J. B.; Duesberg, G. S.; Göritz, A.; Wietstruck, M.; Kaynak, M.,
22 Wafer-Scale Fabrication of Recessed-Channel PtSe₂ MOSFETs With Low Contact
23 Resistance and Improved Gate Control. *IEEE Transactions on Electron Devices* **2018**, *65*
24 (10), 4102-4108.
- 25
26 12. Su, T. Y.; Medina, H.; Chen, Y. Z.; Wang, S. W.; Lee, S. S.; Shih, Y. C.; Chen, C.
27 W.; Kuo, H. C.; Chuang, F. C.; Chueh, Y. L., Phase-Engineered PtSe₂-Layered Films by a
28 Plasma-Assisted Selenization Process toward All PtSe₂-Based Field Effect Transistor to
29 Highly Sensitive, Flexible, and Wide-Spectrum Photoresponse Photodetectors. *Small* **2018**,
30 *14* (19), 10.
- 31
32 13. Yim, C.; Passi, V.; Lemme, M. C.; Duesberg, G. S.; Ó Coileáin, C.; Pallecchi, E.;
33 Fadil, D.; McEvoy, N., Electrical devices from top-down structured platinum diselenide
34 films. *npj 2D Materials and Applications* **2018**, *2* (1), 5.
- 35
36 14. Lin, S.; Liu, Y.; Hu, Z.; Lu, W.; Mak, C. H.; Zeng, L.; Zhao, J.; Li, Y.; Yan, F.;
37 Tsang, Y. H.; Zhang, X.; Lau, S. P., Tunable active edge sites in PtSe₂ films towards
38 hydrogen evolution reaction. *Nano Energy* **2017**, *42*, 26-33.
- 39
40 15. Liu, Y.; Wang, H.; Zhao, W.; Zhang, M.; Qin, H.; Xie, Y., Flexible, Stretchable
41 Sensors for Wearable Health Monitoring: Sensing Mechanisms, Materials, Fabrication
42 Strategies and Features. *Sensors* **2018**, *18* (2).
- 43
44 16. Han, B.; Ou, J., Embedded piezoresistive cement-based stress/strain sensor. *Sensors*
45 *and Actuators A: Physical* **2007**, *138* (2), 294-298.
- 46
47 17. Barlian, A. A.; Park, W.-T.; Mallon, J. R., Jr.; Rastegar, A. J.; Pruitt, B. L., Review:
48 Semiconductor Piezoresistance for Microsystems. *Proc IEEE Inst Electr Electron Eng* **2009**,
49 *97* (3), 513-552.
- 50
51 18. Downey, A.; Laflamme, S.; Ubertini, F.; Sarkar, P., *Experimental damage detection*
52 *of wind turbine blade using thin film sensor array*. SPIE: 2017; Vol. 10168.
- 53
54 19. Iliopoulos, A.; Weijtjens, W.; Van Hemelrijck, D.; Devriendt, C., Fatigue assessment
55 of offshore wind turbines on monopile foundations using multi-band modal expansion. *Wind*
56 *Energy* **2017**, *20* (8), 1463-1479.
- 57
58 20. Fiorillo, A. S.; Critello, C. D.; Pullano, S. A., Theory, technology and applications of
59 piezoresistive sensors: A review. *Sensors and Actuators A: Physical* **2018**, *281*, 156-175.
- 60
21. Obitayo, W.; Liu, T., A Review: Carbon Nanotube-Based Piezoresistive Strain
Sensors. *Journal of Sensors* **2012**, *2012*, 15.
22. Yamada, T.; Hayamizu, Y.; Yamamoto, Y.; Yomogida, Y.; Izadi-Najafabadi, A.;
Futaba, D. N.; Hata, K., A stretchable carbon nanotube strain sensor for human-motion
detection. *Nature Nanotechnology* **2011**, *6*, 296.

23. Amjadi, M.; Pichitpajongkit, A.; Lee, S.; Ryu, S.; Park, I., Highly Stretchable and Sensitive Strain Sensor Based on Silver Nanowire–Elastomer Nanocomposite. *ACS Nano* **2014**, *8* (5), 5154-5163.
24. Lee, J.; Kim, S.; Lee, J.; Yang, D.; Park, B. C.; Ryu, S.; Park, I., A stretchable strain sensor based on a metal nanoparticle thin film for human motion detection. *Nanoscale* **2014**, *6* (20), 11932-11939.
25. Cui, C.; Xue, F.; Hu, W.-J.; Li, L.-J., Two-dimensional materials with piezoelectric and ferroelectric functionalities. *npj 2D Materials and Applications* **2018**, *2* (1), 18.
26. Manzeli, S.; Allain, A.; Ghadimi, A.; Kis, A., Piezoresistivity and Strain-induced Band Gap Tuning in Atomically Thin MoS₂. *Nano Letters* **2015**, *15* (8), 5330-5335.
27. Smith, A. D.; Niklaus, F.; Paussa, A.; Vaziri, S.; Fischer, A. C.; Sterner, M.; Forsberg, F.; Delin, A.; Esseni, D.; Palestri, P.; Östling, M.; Lemme, M. C., Electromechanical Piezoresistive Sensing in Suspended Graphene Membranes. *Nano Letters* **2013**, *13* (7), 3237-3242.
28. Wagner, S.; Yim, C.; McEvoy, N.; Kataria, S.; Yokaribas, V.; Kuc, A.; Pindl, S.; Fritzen, C.-P.; Heine, T.; Duesberg, G. S.; Lemme, M. C., Highly Sensitive Electromechanical Piezoresistive Pressure Sensors Based on Large-Area Layered PtSe₂ Films. *Nano Letters* **2018**, *18* (6), 3738-3745.
29. Biccari, S.; Boland, C. S.; O'Driscoll, D. P.; Harvey, A.; Gabbett, C.; O'Suilleabhain, D. R.; Griffin, A. J.; Li, Z.; Young, R. J.; Coleman, J. N., Negative Gauge Factor Piezoresistive Composites Based on Polymers Filled with MoS₂ Nanosheets. *ACS Nano* **2019**.
30. Kandemir, A.; Akbali, B.; Kahraman, Z.; Badalov, S. V.; Ozcan, M.; Iyikanat, F.; Sahin, H., Structural, electronic and phononic properties of PtSe₂: from monolayer to bulk. *Semiconductor Science and Technology* **2018**, *33* (8), 085002.
31. Wang, Z. G.; Li, Q.; Besenbacher, F.; Dong, M. D., Facile Synthesis of Single Crystal PtSe₂ Nanosheets for Nanoscale Electronics. *Advanced Materials* **2016**, *28* (46), 10224-10229.
32. Smith, A. D.; Niklaus, F.; Paussa, A.; Schröder, S.; Fischer, A. C.; Sterner, M.; Wagner, S.; Vaziri, S.; Forsberg, F.; Esseni, D.; Östling, M.; Lemme, M. C., Piezoresistive Properties of Suspended Graphene Membranes under Uniaxial and Biaxial Strain in Nanoelectromechanical Pressure Sensors. *ACS Nano* **2016**, *10* (11), 9879-9886.
33. Hosseini, M.; Elahi, M.; Pourfath, M.; Esseni, D., Very large strain gauges based on single layer MoSe₂ and WSe₂ for sensing applications. *Applied Physics Letters* **2015**, *107* (25), 253503.

Supporting Information

PtSe₂ grown directly on polymer foil for use as a robust piezoresistive sensor

Conor S. Boland*, Cormac Ó Coileáin, Stefan Wagner, John B. McManus, Conor P. Cullen,
Max C. Lemme, Georg S. Duesberg and Niall McEvoy*

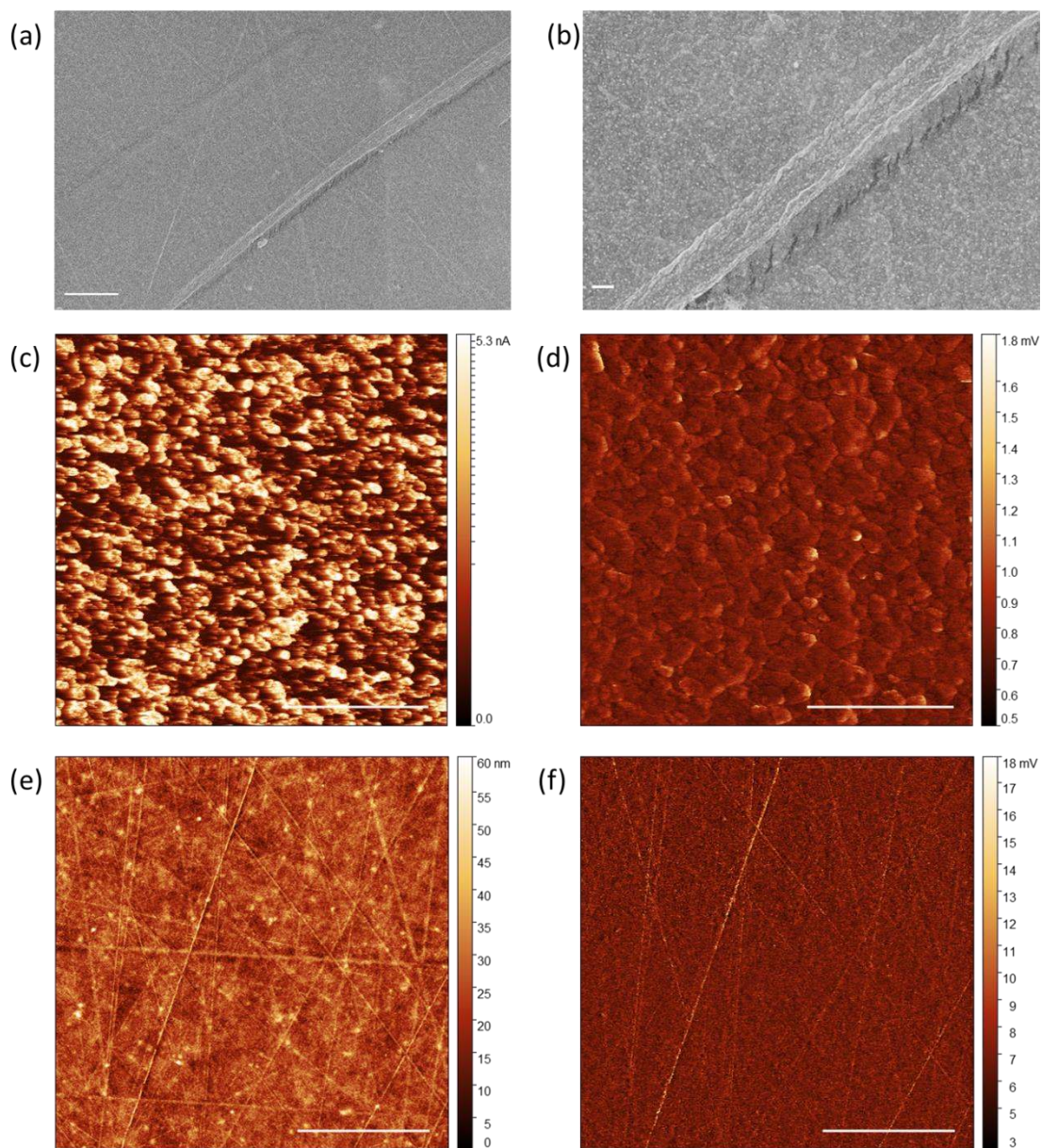


Figure S1:(a, b) Low-magnification SEM images of PtSe₂ from 1 nm Pt on polyimide. Scale bars are 2 μm and 200 nm, respectively. (c, d) Corresponding contact current and deformation AFM images for height image in Figure 1(d) of main text (scale bar = 500 nm). (e, f) Corresponding height and deformation AFM images for contact-current image in Figure 1(e) of main text (scale bar = 10 μm).

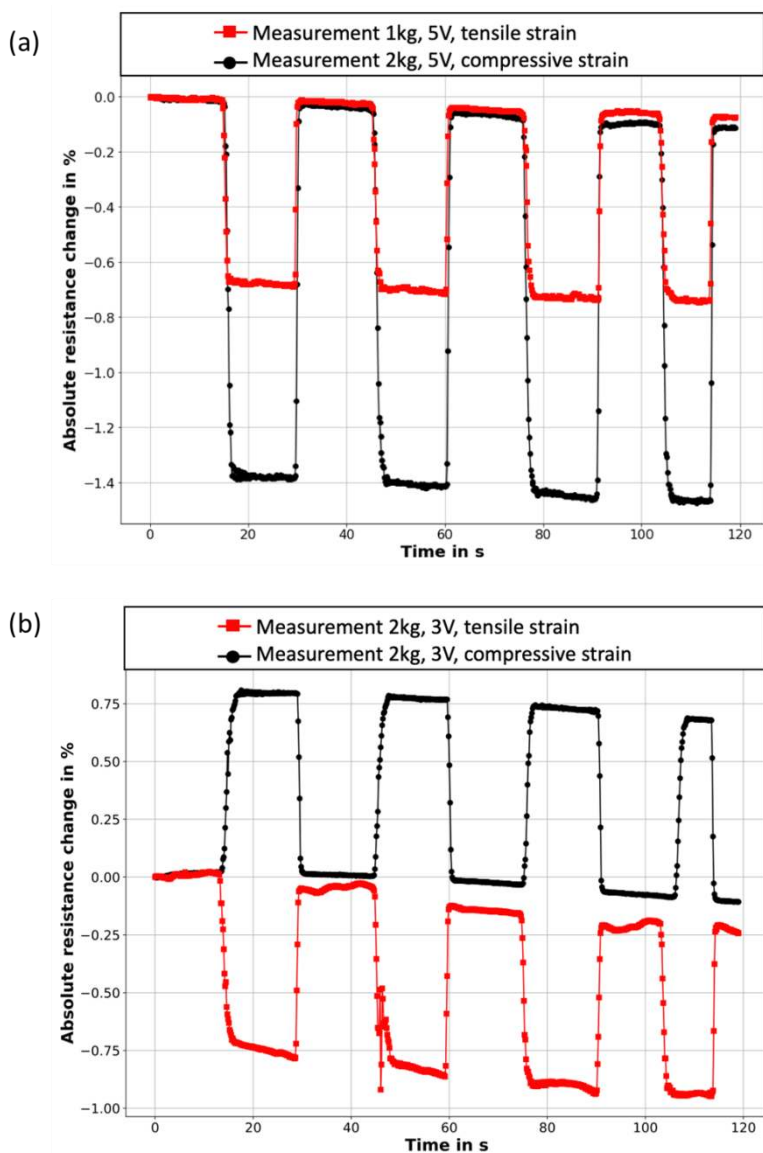


Figure S2: Cantilever bending-beam measurements. (a) Shown is the resistance change of a PtSe₂ on polyimide film grown from 1 nm Pt upon the application of 1 kg and 2 kg masses in a cantilever bending beam setup. This was measured under an applied voltage of 5 V with a cycle duration of 15 s. The extracted gauge factor is ~-30 which is lower than, but of the same order of magnitude as, transferred PtSe₂ films previously measured in a similar setup. (b) Measurements of the same film under compressive and tensile strain with a 2 kg mass and an applied voltage of 3 V.

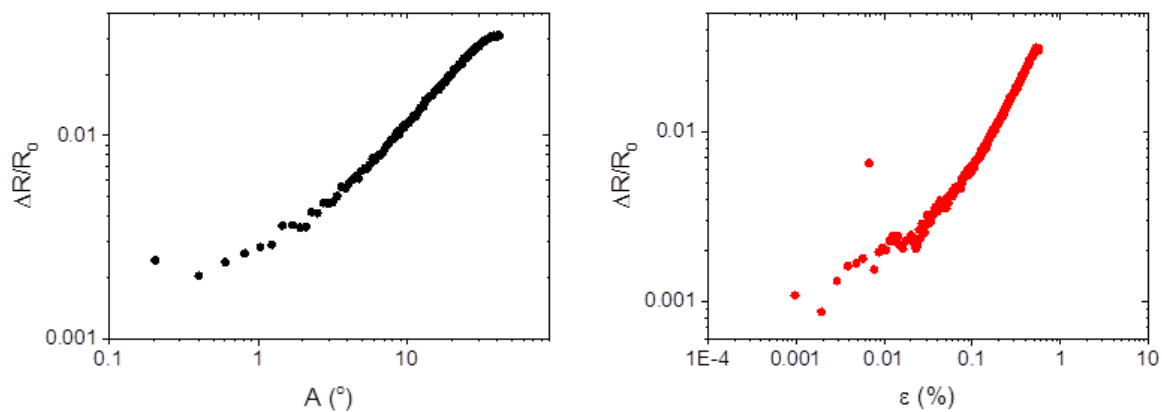


Figure S3: Electromechanical response of reference 1 nm Pt film on polyimide (not selenised). This shows an increase in resistance under applied strain, leading to a positive gauge factor, as expected for a metal.

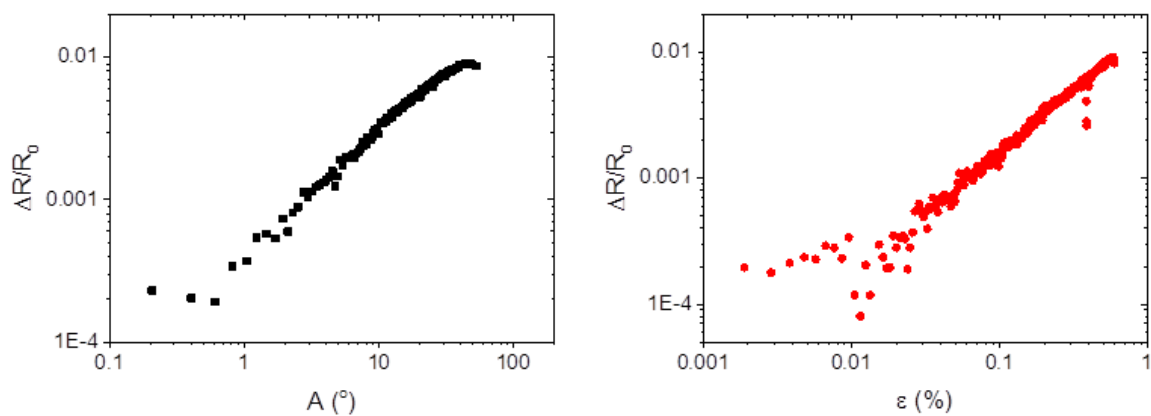


Figure S4: Electromechanical response of 1 nm Pt film on polyimide which was sulfurised rather than selenised. Under the reaction conditions used the formation of PtS is expected. This shows an increase in resistance under applied strain, giving rise to a positive gauge factor.

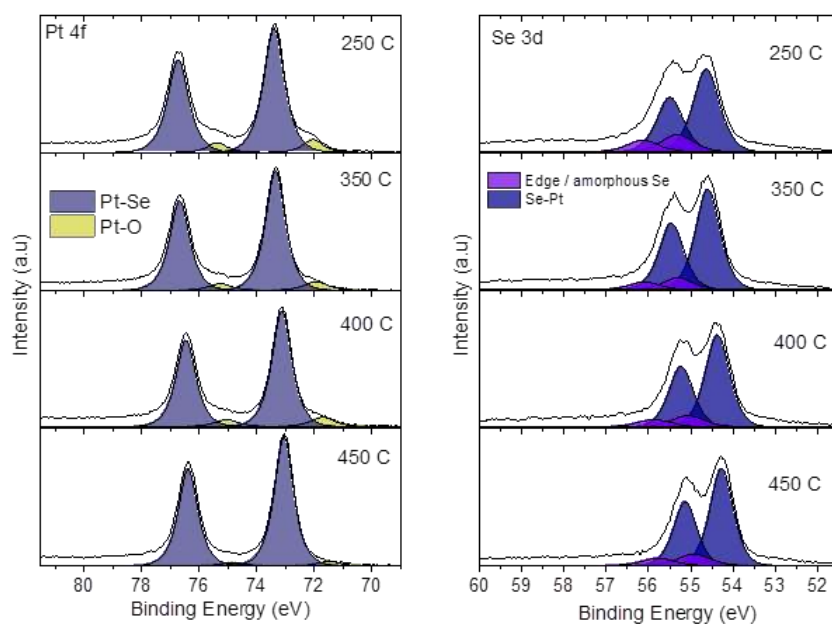


Figure S5: Pt 4f and Se 3d core level spectra of PtSe₂ films grown from 1 nm Pt on polyimide at different temperature.

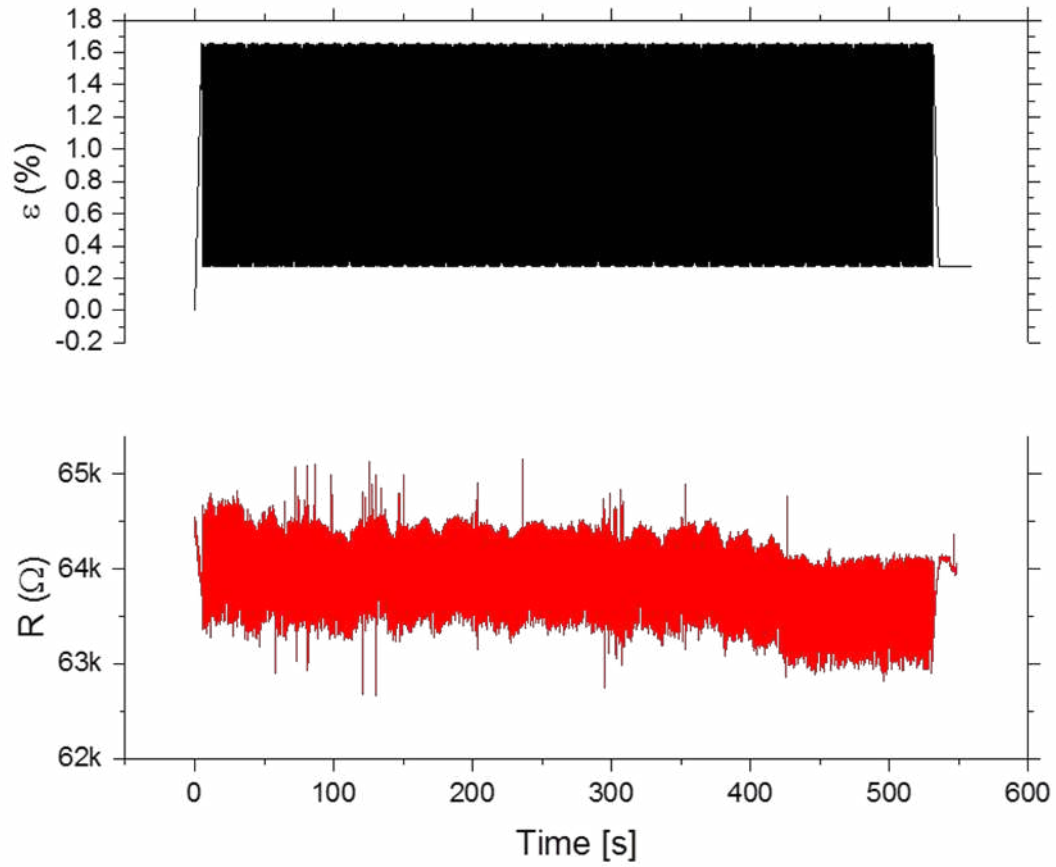
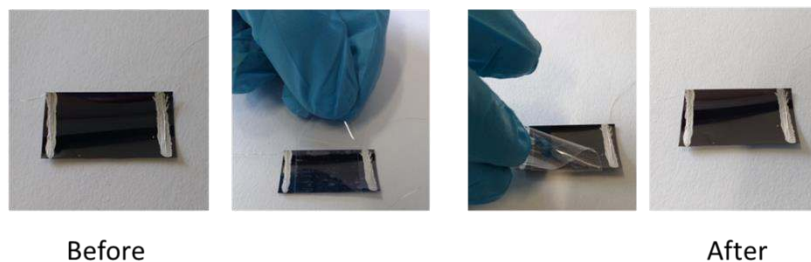


Figure S6: Repeated cycling of PtSe₂ on polyimide (from 1 nm Pt film) shown in Figure 4(a) of main manuscript.

Peel Testing



Solvent Soak

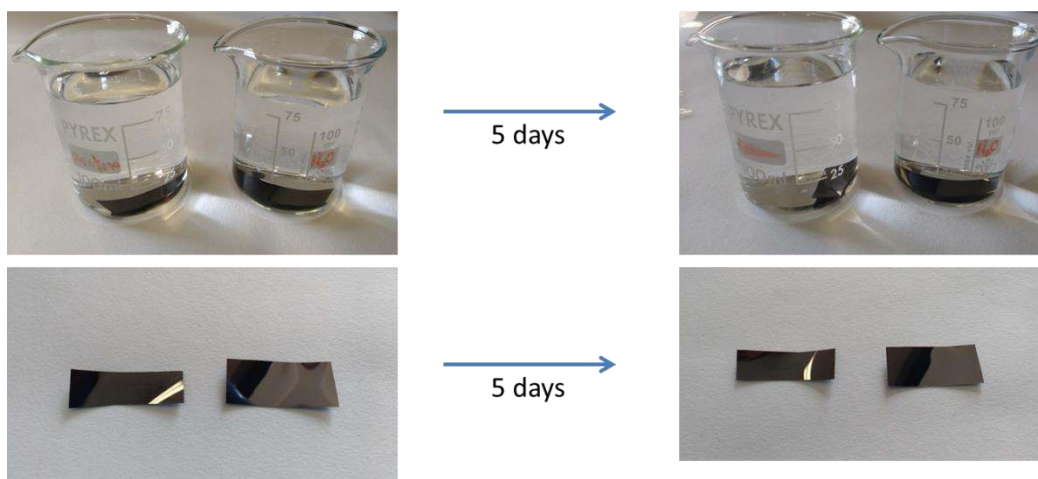


Figure S7: **Peel testing:** 1 nm Pt thickness film sample has tape applied and peeled off 50 times. Different piece of tape for each peel is used. **Solvent soak:** 1 nm Pt thickness film sample cut into two pieces is soaked in deionised water and acetone for 5 days. Solvent is replenished each day.

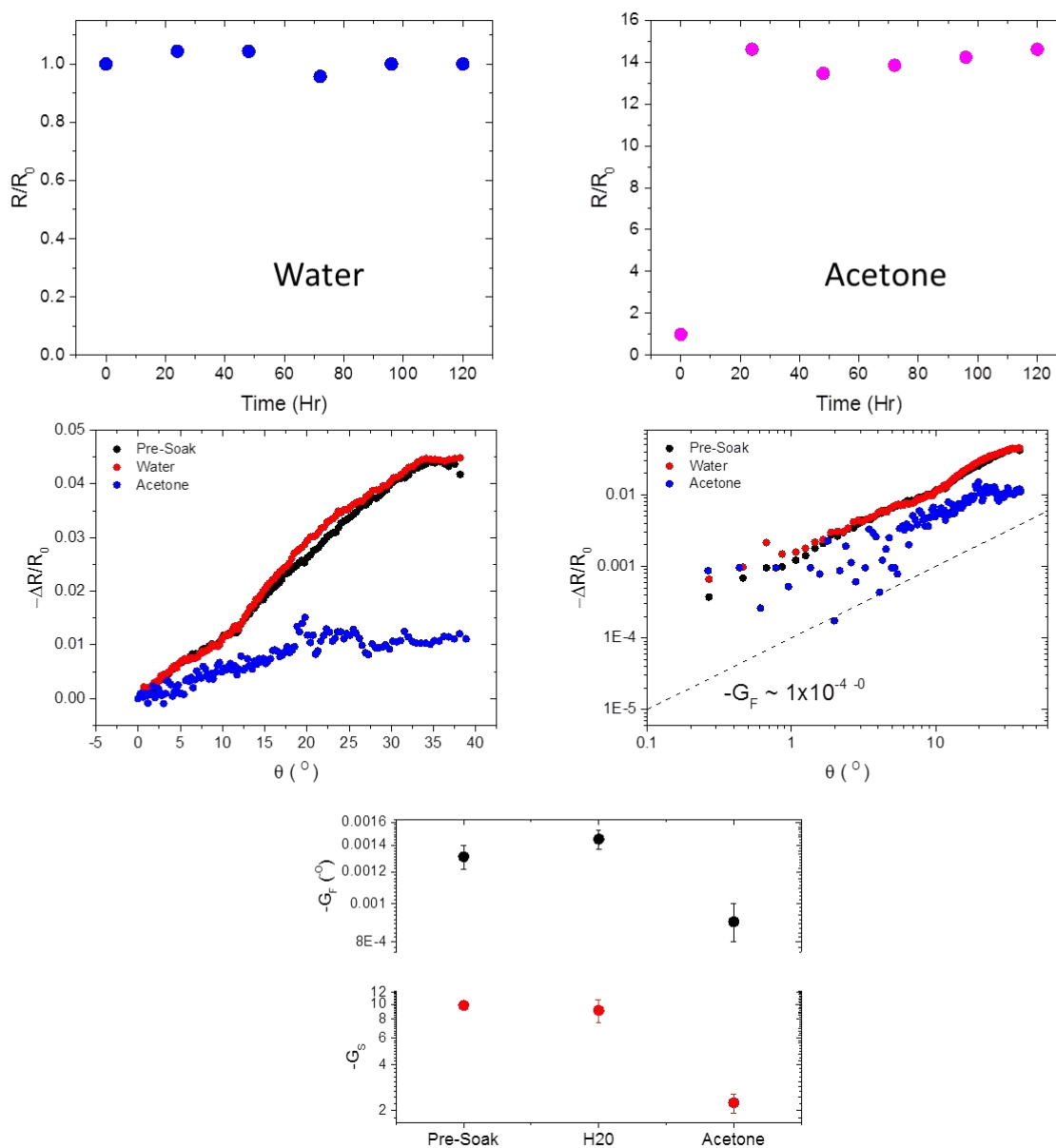


Figure S8. Additional data for solvent soaked samples. The soaked samples were PtSe₂ from 1 nm Pt on polyimide converted at 400 °C (a, b) Change in resistance over time due to immersion in water and acetone. (c, d) Effect of solvent soak on the change in fractional resistance as a function of applied flexure angle. (e) Extracted gauge factors for pristine sample, water-soaked sample and acetone-soaked sample.