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Out-of-plane Piezoelectricity and Ferroelectricity in Layered α - In_2Se_3 Nano-flakes

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ABSTRACT: Piezoelectric and ferroelectric properties in the two dimensional (2D) limit are highly desired for nanoelectronic, electromechanical, and optoelectronic applications. Here we report the first experimental evidence of out-of-plane piezoelectricity and ferroelectricity in van der Waals layered α - In_2Se_3 nano-flakes. The non-centrosymmetric R3m symmetry of the α - In_2Se_3 samples is confirmed by scanning transmission electron microscopy, second-harmonic generation, and Raman spectroscopy measurements. Domains with opposite polarizations are visualized by piezo-response force microscopy. Single-point poling experiments suggest that the polarization is potentially switchable for α - In_2Se_3 nano-flakes with thicknesses down to ~ 10 nm. The piezotronic effect is demonstrated in two-terminal devices, where the Schottky barrier can be modulated by the strain-induced piezopotential. Our work on polar α - In_2Se_3 , one of the model 2D piezoelectrics and ferroelectrics with simple crystal structures, shows its great potential in electronic and photonic applications.

KEYWORDS: In_2Se_3 , 2D materials, piezoelectric, ferroelectric, polarization

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Two-dimensional (2D) van der Waals (vdW) materials encompassing a broad range of novel electronic,^{1, 2} magnetic,³ thermal,^{4, 5} and optical properties^{6, 7} have attracted substantial research interest over the past decade, promising the development of next-generation multifunctional devices. Among various functionalities, piezoelectricity and ferroelectricity widely exploited for the applications in memories,⁸ capacitors,⁹ actuators¹⁰ and sensors¹¹ are relatively scarce in 2D materials. In 2H-stacking transitional metal dichalcogenides (TMDs) such as MoS₂, the inversion symmetry in bulk crystals is broken in ultrathin flakes with odd number of layers, leading to the in-plane piezoelectricity that has been theoretically predicted and experimentally demonstrated¹²⁻¹⁴. Recently, spontaneous in-plane polarization has also been reported in monolayer group IV monochalcogenides¹⁵⁻¹⁷. However, in device applications, out-of-plane piezoelectricity and ferroelectricity are more straightforward for circuit designs. To date, CuInP₂S₆ remains the only known vdW ferroelectric with out-of-plane polarization, although the crystal structure is rather complicated and the polarization is only switchable for films above 4 nm¹⁸⁻²¹. Since traditional ultrathin ferroelectric films such as PbTiO₃ and BaTiO₃ are plagued by dangling bonds and dead layers at the ferroelectric/metal interfaces⁹, it is of great interest to explore new out-of-plane polarized 2D ferroelectrics for non-volatile memory and photovoltaic applications, as well as to enable 2D vdW heterostructures with novel functionalities²²⁻²⁵.

2D out-of-plane ferroelectricity is highly nontrivial, as the depolarization field due to the lack of screening charges may strongly suppress spontaneous polarization in vdW materials. In a recent report, Ding et al. predicted that the layered semiconducting indium selenide (α -In₂Se₃) is a room-temperature out-of-plane polarized ferroelectric down to the single-layer limit (thickness \sim 1 nm), with a calculated electric dipole of 0.11 eÅ/unit cell²⁶. In₂Se₃ has been widely explored for phase-change memory, thermoelectric, and photoelectric applications.^{27, 28} Owing to its

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3 polymorphism and complicated phase diagram, however, even the crystal structure of the
4 thermodynamically stable phase at the room temperature (commonly denoted as α - In_2Se_3)
5 remains controversial.²⁹⁻³¹ Here we report the first experimental observation of out-of-plane
6 piezoelectricity and ferroelectricity in multi-layer α - In_2Se_3 . Using a combination of transmission
7 electron microscopy (TEM), second-harmonic generation, Raman spectroscopy, and piezo-force
8 microcopy (PFM), we show that our In_2Se_3 samples exhibit the rhombohedral R3m structure (Fig.
9 1a), which is non-centrosymmetric and supports the presence of a spontaneous polarization that
10 is potentially switchable by an external bias. The piezotronic effect is demonstrated in that the
11 charge transport in a prototypical device can be modulated by the piezoelectricity. Our work
12 highlights the potential of 2D piezoelectric and ferroelectric materials for novel applications such
13 as sensors, flexible electronics, and nano-electromechanical systems.
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30 In this study, In_2Se_3 nano-flakes prepared by mechanical exfoliation onto conducting
31 substrates and vapor-phase deposition (VPD) on flexible mica substrates are both studied³². Both
32 types of samples have undergone a slow thermal annealing process before the characterizations
33 (see Methods). In order to elucidate the out-of-plane structure of these nano-flakes, we use
34 aberration corrected scanning transmission electron microscopy (AC-STEM) to directly image
35 the cross sections of VPD-grown multi-layer nano-flakes. As shown in Fig. 1b, the cross-
36 sectional samples are fabricated by focused-ion beam (FIB) cutting along the [120] and [100]
37 axes of In_2Se_3 nano-flakes, respectively. From the annular bright-field (ABF) STEM image taken
38 on the [120] cross-section (Fig.1c), the vdW gaps (in bright contrast) are clearly visible between
39 the Se(1)-In(2)-Se(3)-In(4)-Se(5) quintuple layers. Interestingly, the ABF-STEM intensity
40 profile in Fig. 1d indicates that the Se(3) atom is shifted off-center towards the neighboring In(2)
41 atom, which breaks the inversion symmetry of each quintuple layer and gives rise to an out-of-
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3 plane dipole. This observation is consistent with the theoretical calculation²⁶. The high angle
4 annular dark field (HAADF) image and the ABF image along the [100] direction are shown in
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plane dipole. This observation is consistent with the theoretical calculation²⁶. The high angle annular dark field (HAADF) image and the ABF image along the [100] direction are shown in Supplementary Information Fig. S1. The STEM images and structural analysis suggest that the crystal structure of our In₂Se₃ nano-flakes follows the R3m symmetry^{33,34}. We note that α -In₂Se₃ samples in the R-3m or P6₃/mmc symmetry groups have also been reported in the literature^{28,30,35}. While the origin of this discrepancy is not clear and may subject to future investigations, it is possible that the slow annealing pre-treatment is responsible for the polar structure observed in our samples.

The symmetry of our α -In₂Se₃ flakes is further explored by optical second-harmonic generation (SHG). Here a Ti: Sapphire femtosecond-pulsed laser with wavelength $\lambda_{\text{ex}} = 798$ nm generates second-harmonic (SH) signals in reflection. Figure 2a compares the SH spectral intensity ($\lambda = 399$ nm, all polarizations) generated by s-polarized incident laser from a vapor-phase deposited thin flake (thickness $t = 2$ nm) with the 10-fold stronger SH peak that an identical pulse generates from an exfoliated thick flake ($t \sim 100$ nm). These SH signals are, respectively, ~ 70 and ~ 350 times stronger than an identical pulse generates in reflection from a 2 nm thick GaAs film. Moreover, s-polarized SHG (Figure 2b), which has no contribution from the surface, is nearly as strong (averaged over azimuthal angles) as the p-polarized signal (Figure 2c), for which a surface contribution is allowed in principle. Note that VPD grown flakes with thickness from monolayer to four-layer all exhibit prominent SHG intensity (Fig. S3). These observations show that the SHG signal originates from the non-centrosymmetric bulk α -In₂Se₃ crystal, rather than from the broken inversion symmetry at the surface³⁶. The result differs significantly from that of layered MoS₂, where SH intensities are negligible in even-layer and bulk samples due to the restoration of inversion symmetry^{37,38}. The azimuthal angle dependence

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3 of the SHG intensity is also measured on the VPD sample. For the R3m symmetry, SHG
4 intensities take the form I (s-in/s-out) = $I_0 \cos^2(3\theta)$ and I (s-in/p-out) = $I_0 (A+B \cdot \cos(3\theta))^2$ in each
5 polarization configuration. Here θ is the azimuthal angle from [120] direction, and I_0 , A, and B
6 are constants determined by Fresnel coefficients and the nonlinear susceptibility tensor. As
7 shown in Figs. 2b and 2c, the calculated responses fit well to the s-(Figure 2b) and p-polarized
8 (Figure 2c) SHG data in each configuration. In s-in/s-out configuration, only one component of
9 the susceptibility tensor, χ_{yyy} , generates the SH signal; in s-in/p-out configuration, the out-of-
10 plane component, χ_{zyy} , also contributes to the signal. The SHG data are therefore consistent with
11 the conclusion that the symmetry group of our α -In₂Se₃ crystals is R3m.
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25 The broken inversion symmetry and polar structure in In₂Se₃ do not ensure its
26 ferroelectricity, which necessarily requires the presence of a spontaneous polarization that is
27 switchable under external electric fields. In order to investigate the piezoelectricity and
28 ferroelectricity of the α -In₂Se₃ samples, PFM measurements (see Methods) have been carried out.
29 Figure 3a shows the atomic force microscopy (AFM) image of a thick (> 100 nm) exfoliated
30 In₂Se₃ flake with atomically smooth terraces. The out-of-plane PFM phase and amplitude images
31 in Fig. 3b and 3c show two distinct regions with 180° phase difference, corresponding to
32 domains with up and down polarization vectors perpendicular to the flake surface; whereas the
33 domain walls appear as darker lines in the PFM amplitude image (Fig. 3c). Thinner flakes with
34 thicknesses ranging from 3 nm to 60 nm (Fig. 3d) are also exfoliated onto gold substrates for
35 PFM studies. As shown in Figs. 3e and 3f, clear out-of-plane domains can be observed. It is
36 worth noting that some but not all of the domain walls coincide with the location of the flake
37 edges, which suggests that the PFM phase contrasts are more likely coming from real
38 polarization contribution rather than other artifacts between different layers. Unlike CuInP₂S₆,
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3 the In_2Se_3 flake does not display an obvious thickness dependence on the PFM amplitude
4 contrast, which is consistent with the theoretical calculations²⁷. To rule out the possibility that the
5 PFM contrast is caused by the coexistence of different phases, local Raman spectroscopy is
6 performed in this sample at different locations (marked with numerical labels in Fig. 3e), with
7 the corresponding Raman spectra shown in Fig. 3g. Three prominent peaks, A(LO+TO) mode at
8 104 cm^{-1} and A(LO) mode at 182 and 203 cm^{-1} , can be observed at locations 2-6. (Note that the
9 regions with $t = 3\text{ nm}$ might have been oxidized by the Raman excitation laser.) The Raman
10 frequencies are distinctly different from those of another room-temperature stable phase (β
11 phase), with A(LO+TO), A(TO), and A(LO) Raman modes centered at $\sim 110\text{ cm}^{-1}$, $\sim 175\text{ cm}^{-1}$ and
12 $\sim 205\text{ cm}^{-1}$, respectively^{30, 39}. In accordance with previous Raman work,³¹ the presence of the
13 A(LO) mode indicates a lack of inversion symmetry in the R3m structure, consistent with the
14 aforementioned STEM and SHG data.
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32 We have also performed PFM tip poling experiments to study the ferroelectric hysteresis
33 behavior of $\alpha\text{-In}_2\text{Se}_3$. Unfortunately, due to the small bulk resistivity, significant leakage current
34 usually takes place before the switching events across the entire sample. Fig. S4 shows the I-V
35 characteristics across a 15-nm-thick In_2Se_3 flake between a $1\text{ }\mu\text{m} \times 1\text{ }\mu\text{m}$ Au pad and the bottom
36 electrode. Substantial leakage current is observed for a bias beyond $\pm 3\text{ V}$, indicative of a large
37 amount of defects (most likely Se vacancies) and charge carriers in the material. Because of the
38 charge screening, we are not able to demonstrate the conventional remnant P-E hysteresis loop
39 by the Sawyer-Tower method⁴⁰. Nevertheless, we show that it is possible to obtain bias-on PFM
40 hysteresis loops at individual points of the In_2Se_3 flakes. An example on a 20-nm-thick sample is
41 seen in Figs. 4a and 4b, where a stiff cantilever with a spring constant of 40 N/m is used and the
42 DC bias voltage is swept between -3 V and $+6\text{ V}$ with an AC voltage of 800 mV . Here the
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3 amplitude response shows a butterfly loop with an opening of ~ 1.5 V, whereas the phase
4 switches 180° at the same turning points. The unsaturated amplitude signal is likely due to the
5 significant leakage (high concentration of free carriers) of the samples, although we cannot
6 exclude the possibility of surface charging effect. The offset of the loop from zero bias is from
7 the Schottky barrier difference between the upper (In_2Se_3 / IrPt tip) and lower (In_2Se_3 / Au
8 substrate) surfaces of the sample. Similar results are acquired on flakes with thicknesses down to
9 ~ 10 nm and the data resemble the hysteresis loops in standard ferroelectrics like PZT (Fig. S5).
10 We emphasize that this extrinsic leakage effect may be mitigated by doping of the opposite type
11 of charged impurities or using a different growth mechanism such as molecular-beam epitaxy
12 (MBE). The same practice, for instance, has been successfully adopted to suppress bulk carriers
13 in the Bi_2Se_3 family of topological insulators^{41, 42}.
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30 Finally, a flexible In_2Se_3 device taking advantage of its out-of-plane piezoelectricity was
31 demonstrated in Fig. 5. Standard photolithography is used to fabricate two-terminal devices on
32 the VPD-grown multi-layer In_2Se_3 flakes (~ 10 nm) on mica substrates. High work-function metal
33 Pd (20 nm) are deposited on the sample surface to form Schottky contacts. As shown in Fig. 5a,
34 the source-drain current increases (decreases) considerably when the In_2Se_3 flake is under a small
35 tensile (compressive) strain of $\pm 0.1\%$. Such a piezotronic effect has been previously reported in
36 zinc oxide thin films⁴³, where the Schottky barrier height is modulated by the bound charges
37 induced by the piezoelectricity of the semiconducting material, as schematically illustrated in
38 Figs. 5b – 5e. Fifteen 2D In_2Se_3 devices have been investigated and all display the same transport
39 characteristics in our experiment, suggesting a robust piezotronic effect that can be utilized for
40 electromechanical energy transduction applications.
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3 To summarize, the out-of-plane piezoelectricity and ferroelectricity in multi-layer α -
4 In_2Se_3 are explored by a combination of structural, optical, and electrical characterizations. The
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6 non-centrosymmetric $R3m$ crystal symmetry is confirmed by STEM, SHG, and Raman
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8 measurements. Ferroelectric domains are clearly visualized by PFM and the out-of-plane
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10 polarization is potentially switchable in samples with ~ 10 nm of thickness. Finally, the
11
12 modulation of charge transport by bending of the substrate has also been demonstrated with a
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14 flexible device with mica substrate, showing great potential for applications in nanoscale
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16 electromechanical devices and piezotronic sensors. With further reduction of the bulk carrier
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18 density, it is possible that ferroelectric In_2Se_3 can be realized down to the single layer limit,
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20 which is highly desirable for memory, sensing, and photovoltaic applications.
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30 Methods

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32 *Sample preparation.* In_2Se_3 nano-flakes were grown on flexible fluorophlogopite mica substrates
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34 via vdW epitaxy in a pressure controllable vapor deposition system equipped with a 1-inch
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36 quartz tube.³² The In_2Se_3 powder source (99.99%, Alfa Aesar) was heated to 690-750 °C at the
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38 center of the tube furnace. The vapor was transported downstream by ~ 50 sccm Ar gas with
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40 pressure controlled at ~ 50 torr. The growth of In_2Se_3 nano-flakes occurred on the mica substrates
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42 placed 7-12 cm away from the heated center. After growth, the chamber was naturally cooled
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44 down to room temperature. Thin flakes were also exfoliated onto Au surface from the bulk taken
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46 out of the growth chamber for PFM measurements.
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52 *STEM.* The cross-section TEM samples were prepared by focused ion beam cutting from two
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54 directions and were characterized by an aberration-corrected and monochromated G2 cubed
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56 Titan 60-300 electron microscope under 60 kV.
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3 *SHG microscopy.* A continuous-wave Ti: Sapphire laser operating at ~ 798 nm, 76 MHz
4 repetition rate, 150 fs pulse duration with *s*-polarization were focused on the sample surface at
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6 incident angle $\theta = 45^\circ$, and SHG signals with *s* or *p*-polarization were collected in a reflection
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8 geometry. A photo-multiplier tube (PMT) with bandpass filters was used to suppress the
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10 fundamental wave. It was confirmed that SHG signals scaled quadratically with the incident
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12 fundamental intensity.
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18 *PFM measurements.* PFM measurements were conducted using a Park XE-70 system equipped
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20 with a Zurich HF2LI lock-in amplifier. P-E hysteresis loops were obtained with Asylum
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22 Research MFP-3D Infinity. Using stiff cantilevers with a spring constant of 40 N/m were used to
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24 eliminate the electrostatic contribution.
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28 *Raman spectroscopy characterization.* Raman spectroscopy was carried out using Witec Alpha
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30 300 micro-Raman confocal microscope with a 488 nm laser excitation. The laser power was
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32 minimized to avoid burning the flakes.
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36 *Device fabrication and measurements.* The flexible In_2Se_3 two-terminal devices were achieved
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38 by standard photolithography process, electron-beam deposition of Pd/Au (20 nm/50 nm) and
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40 gold wire pasted by silver epoxy for external connection. I-V measurements were conducted
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42 with Keithley 4200 Semiconductor Characterization System.
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45 ASSOCIATED CONTENT

46 47 **Supporting Information**

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50 The HAADF TEM images, the setup of SHG, piezoelectricity measurements with devices are
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52 given in this section. This material is available free of charge via the Internet.
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56 AUTHOR INFORMATION

Notes

⁺Y. Zhou and D. Wu contributed equally to this work.

The authors declare no competing financial interest.

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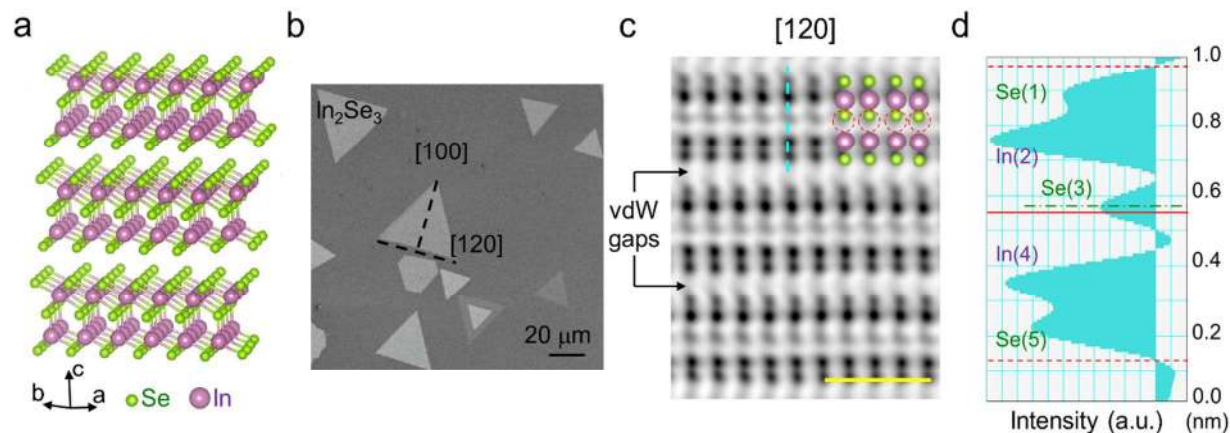


Figure 1. Atomic structure of layered In_2Se_3 nano-flake. (a) Crystal structure of α - In_2Se_3 in space group of $R\bar{3}m$. (b) Scanning electron micrograph (SEM) of VPD grown In_2Se_3 flakes. The [120] and [100] zone axes, along which the flakes are cut for STEM studies, are labeled in the image. (c) Cross-sectional annular bright-field (ABF) STEM image of an In_2Se_3 flake cut along the [120] direction. Se and In atoms, as well as the van der Waals gaps, are indicated in the figure. The scale bar is 1 nm. (d) Intensity profile along the blue dashed line in (c). The center of the Se(3) atom is slightly shifted with respect to the central position of the quintuple layer.

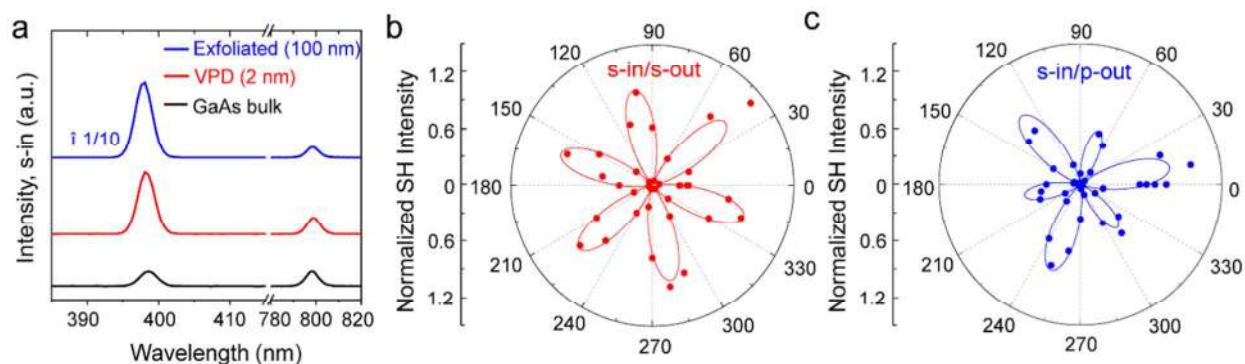


Figure 2. SHG of In_2Se_3 nano-flakes. (a) SH spectral intensity at 399 nm (all polarizations) generated in reflection from VPD grown (red), exfoliated (blue) In_2Se_3 flakes (~ 100 nm thick) and GaAs bulk. All samples are excited by equally intense s-polarized laser pulses with a wavelength of $\lambda_{\text{ex}} = 798$ nm, which is strongly suppressed in the plot with respect to the corresponding SH peak. (b) Dependence of SHG signals on sample azimuthal angle θ in the s-in/s-out configuration. The red curve is a fit to $I = I_0 \cos^2(3\theta)$. (c) θ -dependence of SHG signals in the s-in/p-out configuration. The blue curve is a fit to $I = I_0 (A + B \cdot \cos(3\theta))^2$. The left-hand axes in (b) and (c) denote the radial scale.

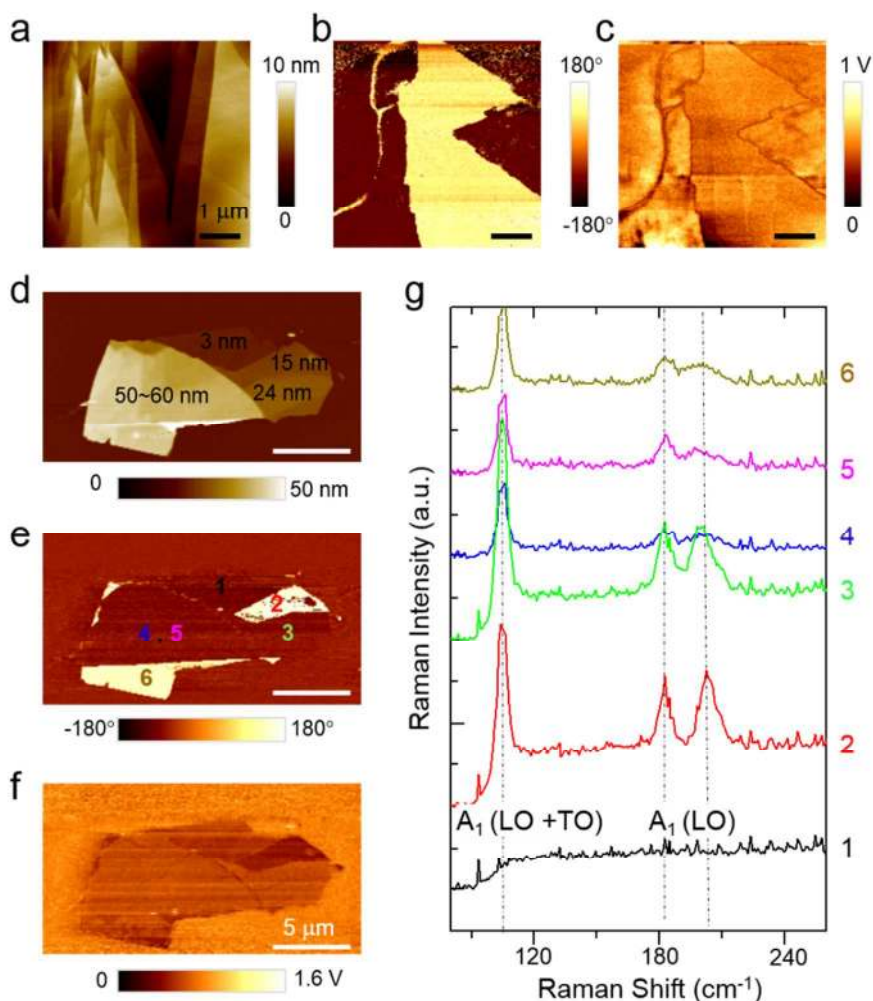


Figure 3| Ferroelectric domains of α - In_2Se_3 flakes. (a - c) AFM, PFM phase and amplitude images of a thin α - In_2Se_3 flake (> 100 nm). (d - f) AFM, PFM phase and amplitude images of a thin α - In_2Se_3 flake exfoliated onto gold surface. The PFM phase contrast of 180° in both samples indicates the presence of different domains with opposite out-of-plane polarizations. The scale bars are $1 \mu\text{m}$ in (a - c) and $5 \mu\text{m}$ in (d - f). (g) Raman spectra at different locations labeled in (d). The prominent Raman peaks at 104 cm^{-1} and $182 / 203 \text{ cm}^{-1}$ are associated with $A(\text{LO} + \text{TO})$ and $A(\text{LO})$ modes, respectively.

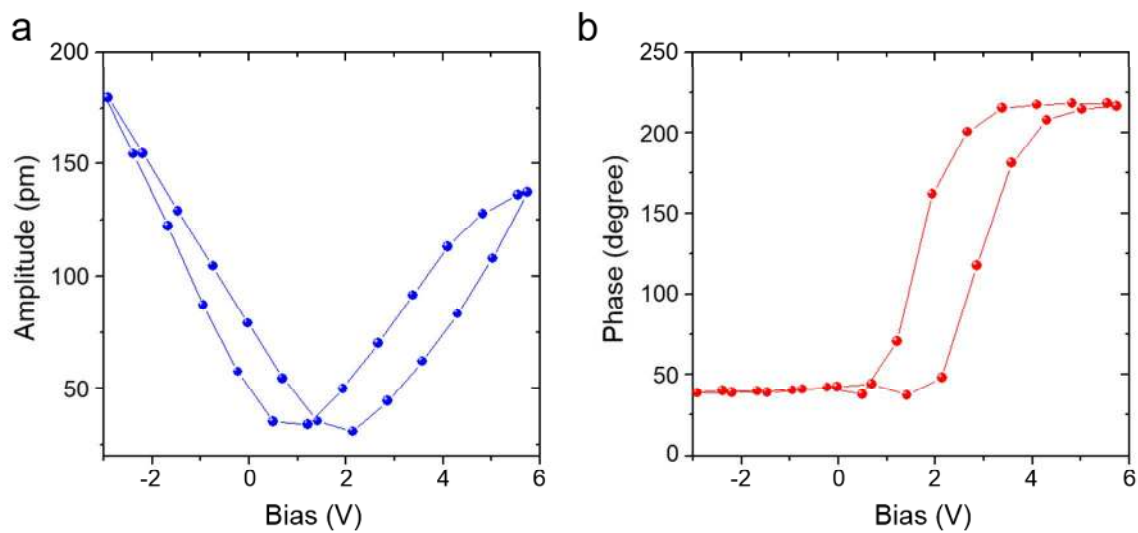


Figure 4| Polarization reversal under external electrical field. On-field (a) PFM amplitude and (b) PFM phase hysteresis loops on a 20-nm-thick flake.

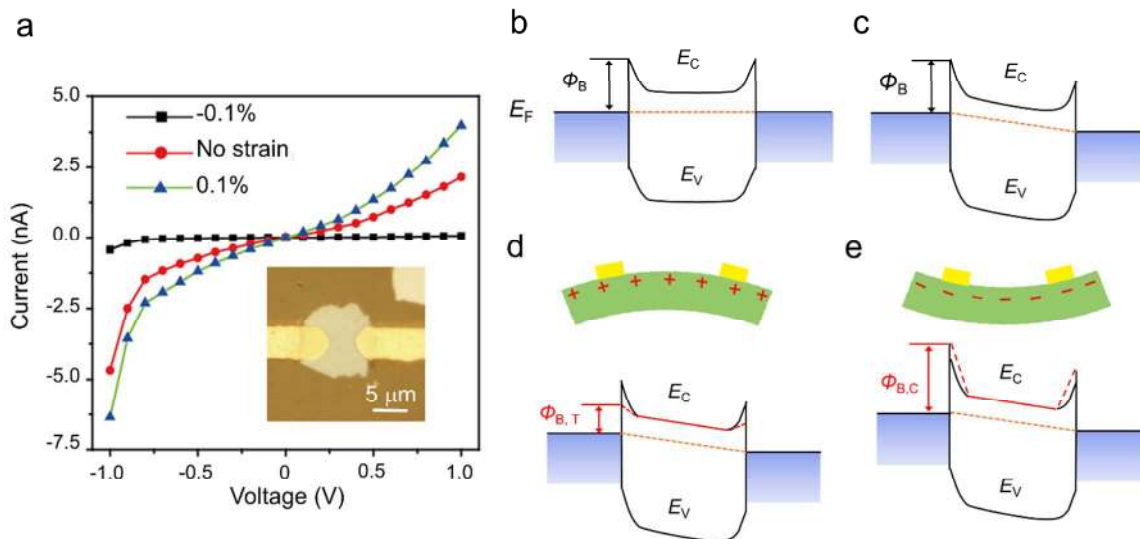


Figure 5. Piezotronic effect on prototypical In₂Se₃ devices. (a) Typical I-V characteristics of two-terminal In₂Se₃ devices under compressive (black), zero (red), and tensile (blue) strains by bending the substrate. Inset shows an image of typical 2D In₂Se₃ device. (b - e) Band diagrams under different conditions: (b) Zero strain with zero source-drain bias. (c) Zero strain with non-zero source-drain bias. (d) Tensile strain with non-zero source-drain bias, resulting in lower Schottky barriers ($\Phi_{B, T}$) and enhanced current. (e) Compressive strain with non-zero source-drain bias, resulting in higher Schottky barriers ($\Phi_{B, C}$) and reduced current.