Supporting Information for
Layer-Dependent Ferroelectricity in 2H-Stacked Few-Layer α-In_2Se_3

Baohua Lv,[a, b, c, ‡] Zhi Yan,[a, c, ‡] Wuhong Xue,[* a, c] Ruilong Yang,[a, c] Jiayi Li,[d] Wenjuan Ci,[a, c] Ruixue Pang,[a, c] Peng Zhou,[d] Gang Liu,[e] Zhongyuan Liu,[f] Wenguang Zhu,[g] and Xiaohong Xu,[* a, c]

[a] School of Chemistry and Materials Science of Shanxi Normal University & Key Laboratory of Magnetic Molecules and Magnetic Information Materials of Ministry of Education, Linfen 041004, China. E-mail: xuxh@sxnu.edu.cn
[b] Department of Applied Chemistry, Yuncheng University, Yuncheng 044000, China.
[c] Research Institute of Materials Science of Shanxi Normal University & Collaborative Innovation, Linfen 041004, China. E-mail: xuewuhong@sxnu.edu.cn
[d] ASIC & System State Key Lab School of Microelectronics, Fudan University, Shanghai 200433, China
[e] School of Electronic Information and Electrical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China
[f] State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, China
[g] International Center for Quantum Design of Functional Materials (ICQD), Hefei National Laboratory for Physical Sciences at the Microscale, and Key Laboratory of Strongly-Coupled Quantum Matter Physics Chinese Academy of Sciences, School of Physical Sciences, University of Science and Technology of China, Hefei, Anhui 230026, China; Key Laboratory of Strongly-Coupled Quantum Matter Physics, University of Science and Technology of China, Hefei, Anhui 230026, China

‡ These authors contributed equally.

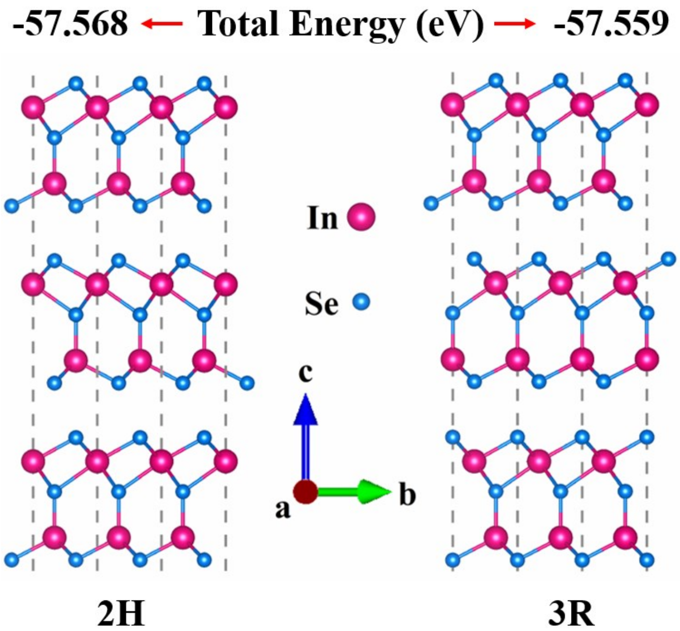
Experimental Section:

Sample Preparation: Large-area high-quality 2D ultrathin 2H-stacked α-In_2Se_3 single crystals were grown on a home-made single temperature zone horizontal furnace equipped with a 1-inch diameter quartz tube under atmospheric pressure. The quartz boat containing In_2Se_3 (99.99 %, Adamas) powders were put in the center of the tube. One slice of fresh-cleaved fluorophlogopite mica sheet was faced downward on the In_2Se_3 source powder. The hermetically-sealed tube was flushed with 1000 sccm N_2 gas for 5 mins to provide oxygen-free environment before heating. In the growth process, N_2 gas was used as the carrier gas with a constant flow rate of 30-80 sccm. The whole reaction process was carried out under the furnace temperature of 750-850 ˚C, and the reaction continued for 5-10 mins. Eventually, the system was naturally cooled down to RT. The In_2Se_3 layers grown on mica substrates could be transferred onto other substrates (Nb-$SrTiO_3$, Pt/Ti/SiO_2/Si and Cu grid) using a PMMA-mediated transfer technique.[1] The In_2Se_3 field effect transistors (FETs) were fabricated by a laser direct-writing (MicroWriter Baby Plus) lithography process followed by thermal evaporation of the Au (80 nm)/Ni (5 nm) electrode metals, and lift-off.

Characterization: The grown In_2Se_3 nanoflakes are characterized by the following means: An optical microcscope (OM, CeWei LW300LJT), a Raman spectroscopy (Horiba LabRAM HR Evolution, 532 nm), an X-ray photoelectron spectroscopy (XPS, Thermo K-Alpha$^+$ with Al K_α radiation as X-ray source for radiation), and a transmission electron microscope (TEM, JEM-2100) with energy-dispersive X-ray spectroscopy (EDX). The cross-sectional high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were acquired by using an aberration corrected FEI Titan Themis 200 at 200 kV with spatial resolutions of 0.08 nm. The TEM samples were fabricated by focused ion beam (FIB, FEI Helios 450S) cutting. The thickness of In_2Se_3 nanosheets was identified using a commercial Atomic Force Microscope (AFM, Bruker Dimension Icon). The intrinsic ferroelectric domain and ferroelectric polarization measurements were carried on a Piezoresponse Force Microscopy (PFM) under resonance-enhanced mode with Pt/Ir tips (spring constant: 3N/m). The OOP and IP piezoelectric signals were acquired at a contact resonance frequency of ~285 kHz and ~686 kHz, respectively. Ferroelectric polarization measurements were conducted using a standardized ferroelectric tester (Precision Multiferroic IcI, Radiant Technologies). *I-V* measurements were performed by Keithley 4200 Semiconductor Analyzer. SHG measurements were conducted in MStarter SHG microscope spectrometer with <1 ps pulse at 1030 nm and a repetition rate of 40 MHz, which was focused to a spot of diameter of ~1um with a 100x objective.

First-Principles Calculations: All In_2Se_3-based structures were fully relaxed in the VASP code.[2, 3] The exchange and correlation functional was treated using the Perdew-Burke-Ernzerhof (PBE) parameterization of generalized gradient approximation (GGA). The Hellmann-Feynman forces on each ion and the energy convergence criterion were set to 0.01 eV/Å and 10^{-5} eV, respectively. A 500 eV plane-wave cutoff energy was used with a Gaussian smearing width of 0.05 eV. The $13 \times 13 \times 1$ k-point meshes were adopted for sampling the Brillouin zone. Van der Waals force was also considered through the DFT-D2 method for multilayer In_2Se_3. The hybrid functional of

Hyed-Scuseria-Ernzerhof (HSE06) was used to calculate the electric polarization. The Berry phase method was used to calculate the in-plane electric polarization. And because of the existence of the vacuum layer, the out-of-plane electric polarization can be calculated by direct integrating ρ times z over the whole supercell, where ρ is the local charge density and z is the coordinate in the out-of-plane axis.



Figures

Fig. S1 The total energy of trilayer 2H- and 3R-stacked α-In_2Se_3 by DFT calculation.

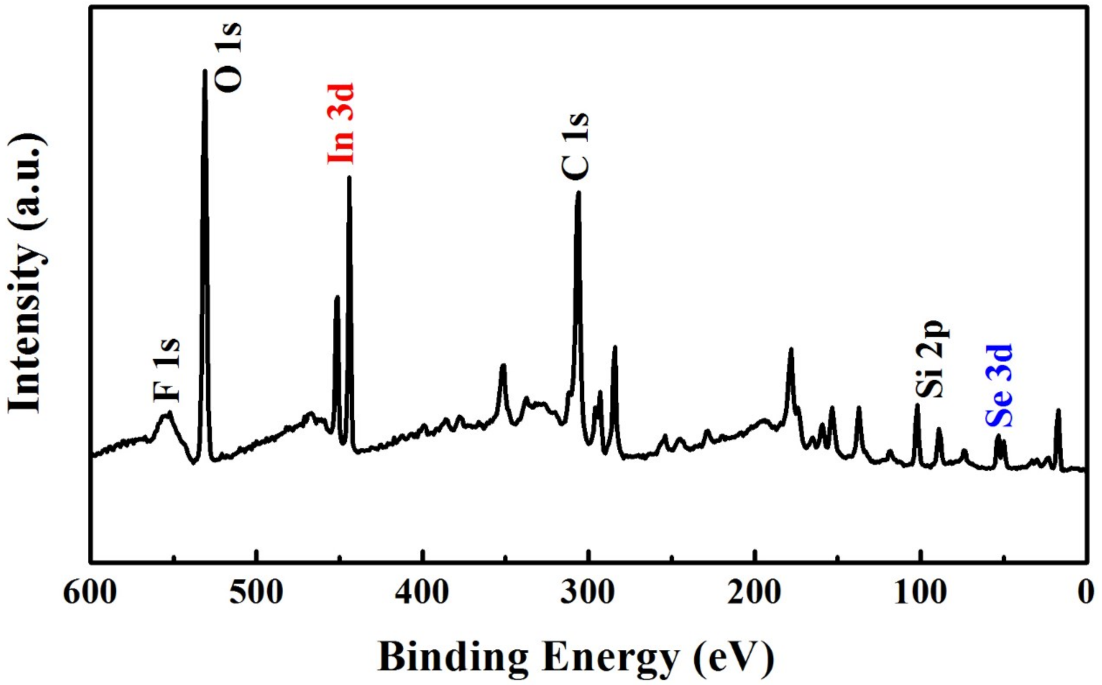


Fig. S2 XPS spectrum of as-grown 2D In_2Se_3 on mica. The result shows an atomic ratio of ~2:3 (2.28 %:5.83 %) for In and Se elements, suggesting good stoichiometry of the grown In_2Se_3. F, O, Si, and C elements come from the mica substrate or the environment.

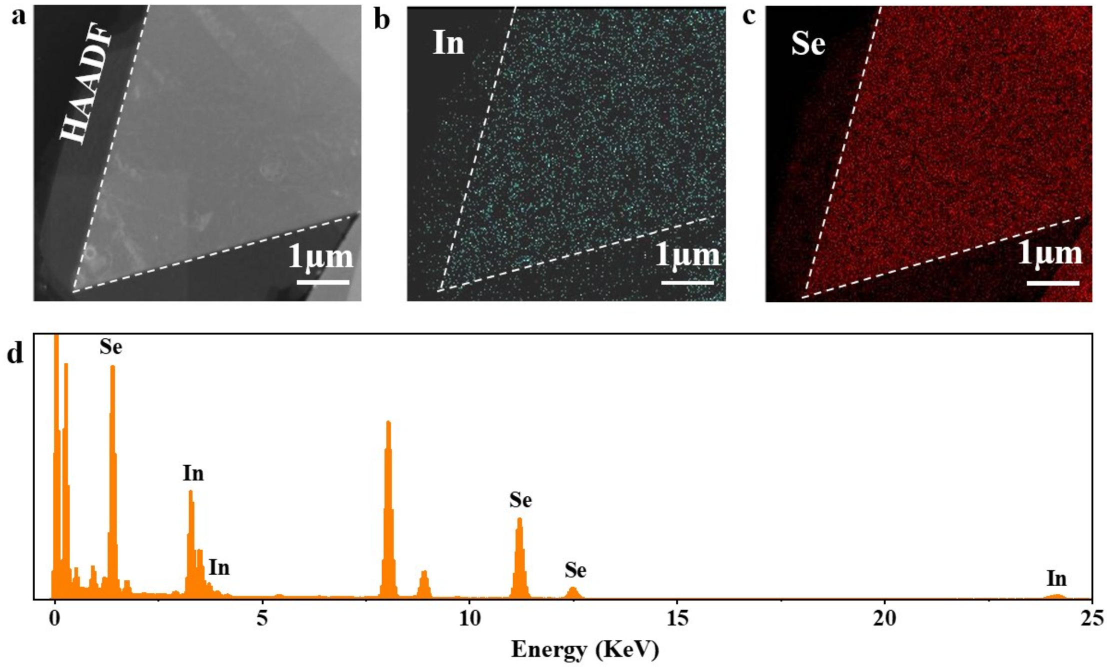


Fig. S3 Element distribution and atomic ratio of the 2D In_2Se_3 nanoflake transferred onto a TEM grid. (a) HAADF image. (b, c) EDS mappings of In and Se. (d) EDS spectrum with In and Se atomic ratio of 2:3.

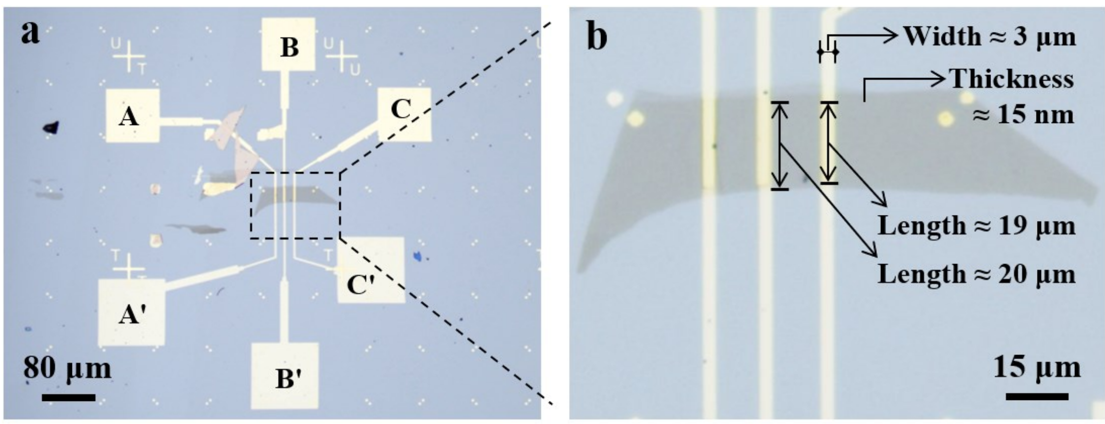


Fig. S4 (a) The optical image of the vertical and lateral 2H α-In_2Se_3 devices for measuring OOP and IP PE loops. The thickness of nanoflake is ~15 nm. The width of electrode is ~3 μm. The channel length and width were ~10 μm and ~20 μm, respectively. The conductive probes were in contact with B´ and C´ to measure IP PE loop and C and C´ for OOP PE loop.

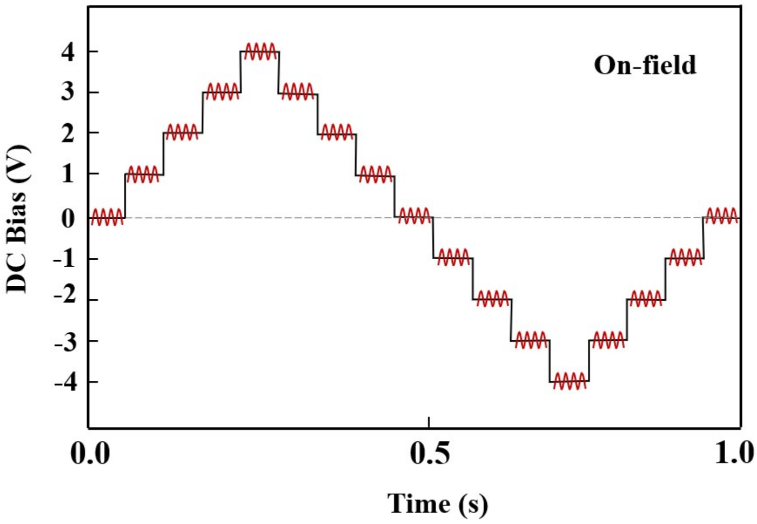


Fig. S5 Waveform of applying voltage for PFM polarization switching with on-field mode under resonance-enhanced PFM mode.

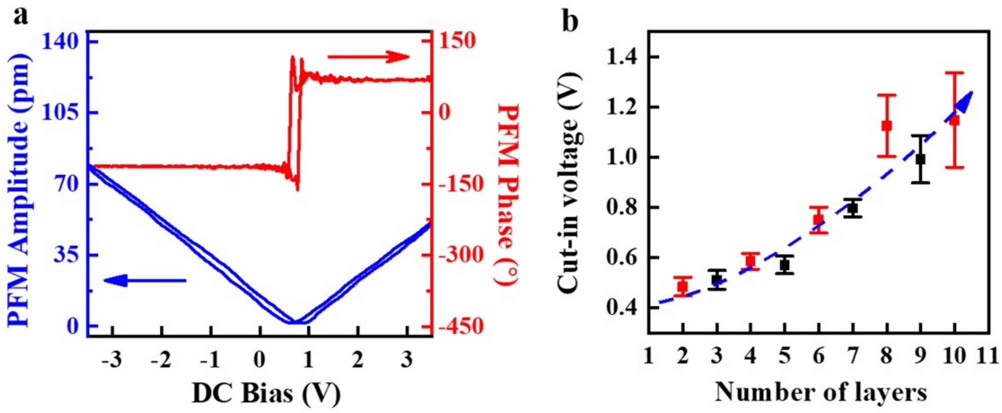


Fig. S6 PFM studies of α-In_2Se_3 nanoflakes transferred onto Nb:$SrTiO_3$. (a) The OOP PFM amplitude and phase hysteresis loop of a 7-nm thick α-In_2Se_3. (b) The OOP cut-in voltages of different layers from 2-10. The data point was acquired from five random positions in each sample.

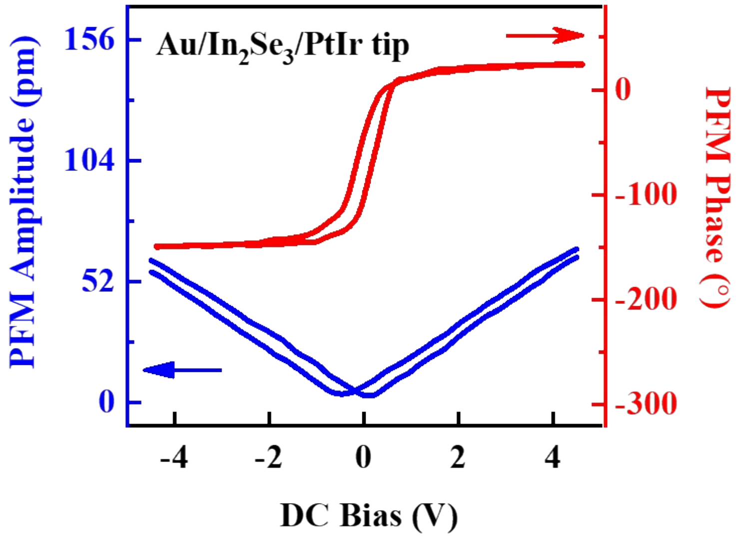


Fig. S7 PFM amplitude (blue) and phase (red) hysteresis loops of 7 nm α-In_2Se flake transferred onto Au electrode.

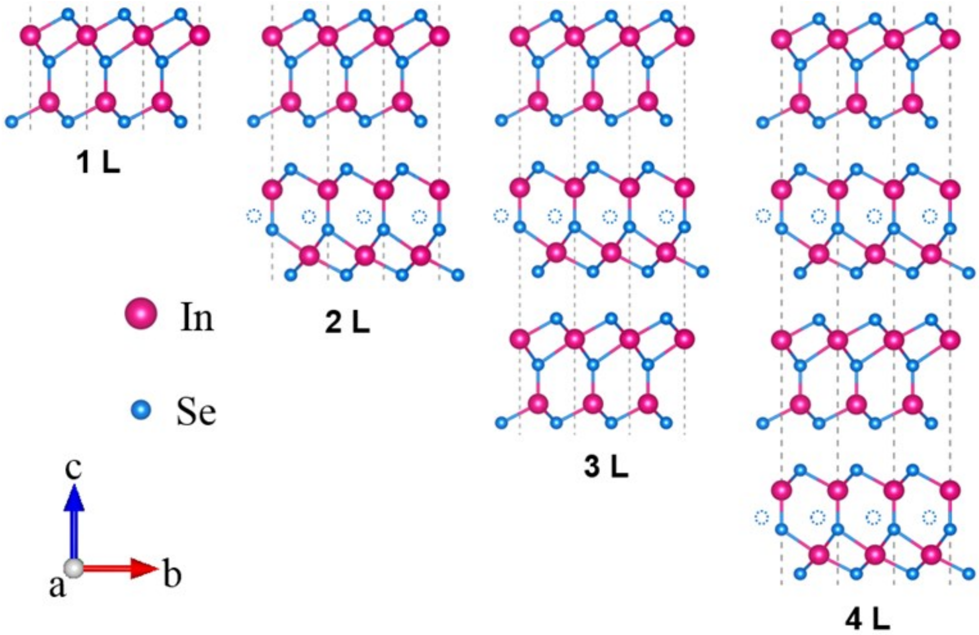


Fig. S8 The structural model of calculating the electric dipoles of the reconstructed structures formed by the shift of the central Se atoms (labeled with dotted circle).

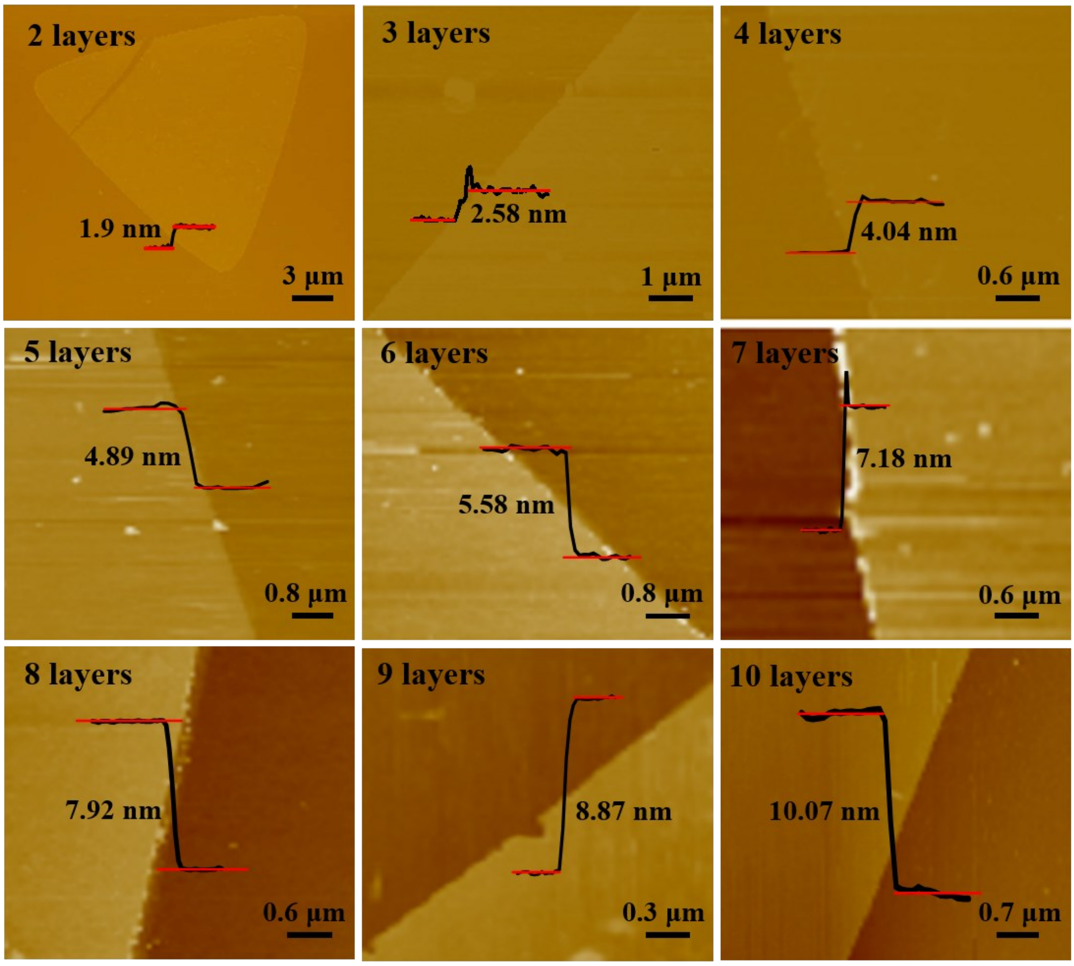


Fig. S9 AFM images for an In_2Se_3 specimen with a thickness ranging from ~2 to 10 nm.

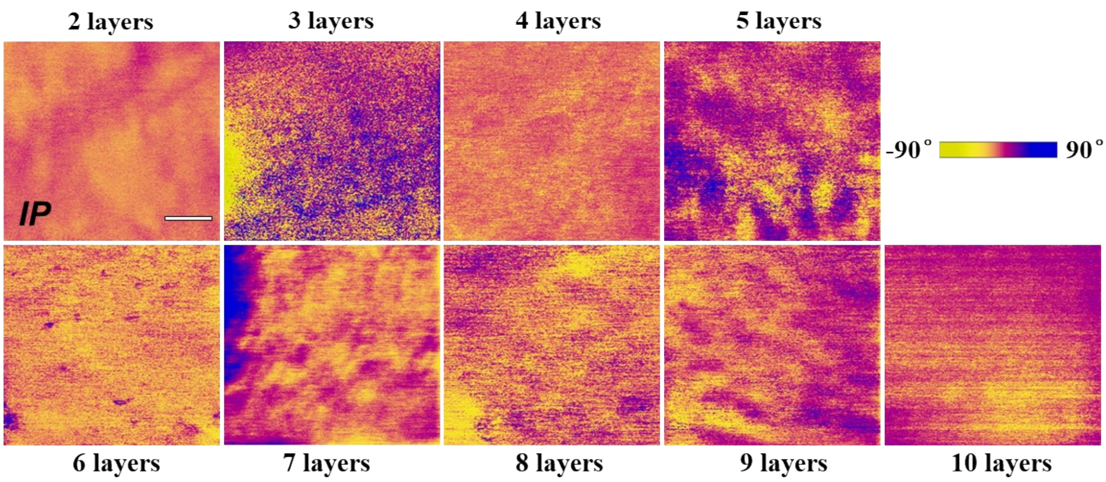


Fig. S10 The IP phase images of 2H-stacked α-In_2Se_3 nanoflakes in the different layers from 2 to 10. Scale bars: 40 nm.

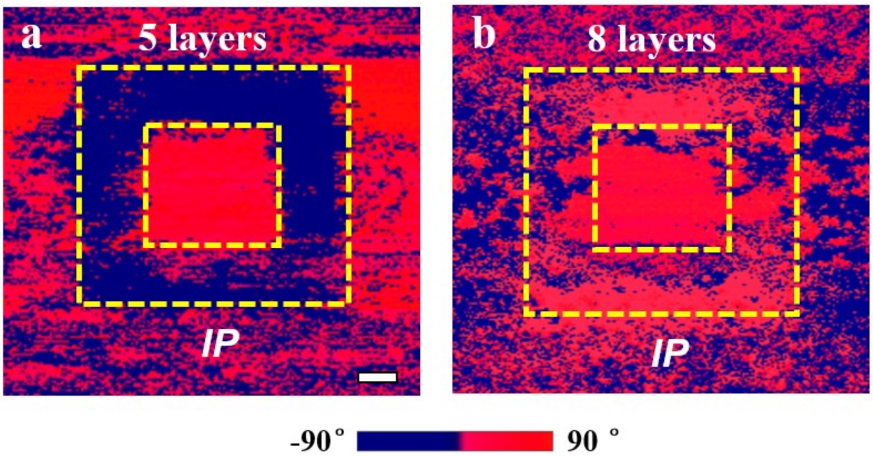


Fig. S11 PFM studies of α-In_2Se_3 nanoflakes transferred onto Pt/Ti/SiO_2/Si. IP PFM phase images of 5 (a) and 8 (b) layered 2H-stacked α-In_2Se_3 nanoflakes after writing the box-in box patterns by applying the forward and reverse DC bias (+5 V for large square and -6 V for small inner square). Scale bars: 500 nm.

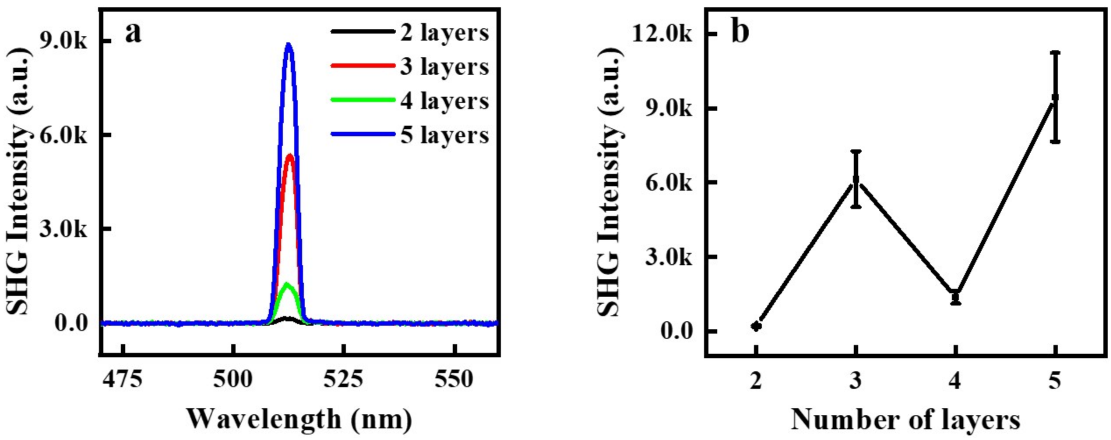


Fig. S12 Layer-dependence of in-plane SHG signals in the 2H α-In_2Se_3 nanoflakes at room temperature. (a) SHG spectral intensity in different layers from 2 to 5. (b) The SHG intensity as a function of the number of layers based on the statistics acquired from five random positions on each thickness nanoflake.

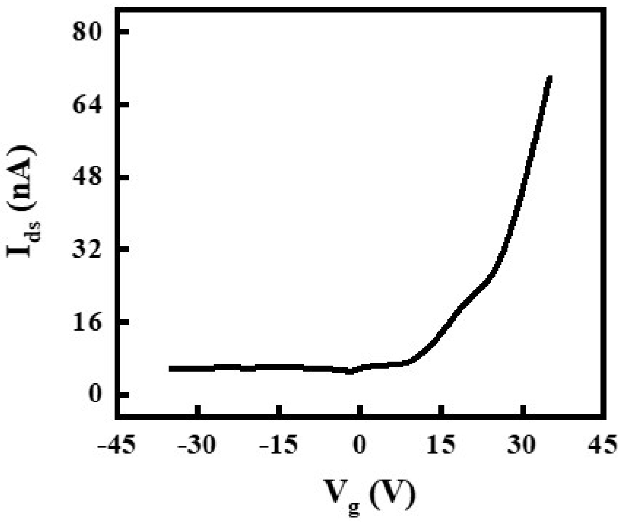


Fig. S13 The transfer curve (I_{ds}-V_g) of the 2H-stacked α-In_2Se_3 based transistor (V_{ds} = 2.5 V) demonstrates the as-prepared α-In_2Se_3 is a typical n-type semiconductor.

References

1 Y. Zhang, J. Chu, L. Yin, T. A. Shifa, Z. Cheng, R. Cheng, F. Wang, Y. Wen, X. Zhan, Z. Wang and J. He, *Adv. Mater.*, 2019, **31**, e1900056.

2 G. Kresse and J. Furthmüller, *Comput. Mater. Sci.*, 1996, **6**, 15-50.

3 G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169-11186.