Supporting Information for
Layer-Dependent Ferroelectricity in 2H-Stacked Few-Layer α-In$_2$Se$_3$

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**Experimental Section:**

**Sample Preparation:** Large-area high-quality 2D ultrathin 2H-stacked $\alpha$-In$_2$Se$_3$ 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$_2$Se$_3$ (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$_2$Se$_3$ 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$_2$Se$_3$ 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$_2$Se$_3$ 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$_2$Se$_3$ nanoflakes are characterized by the following means: An optical microscope (OM, CeWei LW300LJT), a Raman spectroscopy (Horiba LabRAM HR Evolution, 532 nm), an X-ray photoelectron spectroscopy (XPS, Thermo K-Alpha$^+$ with Al K$_\alpha$ 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$_2$Se$_3$ 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 ~1 μm with a 100x objective.

**First-Principles Calculations:** All In$_2$Se$_3$-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$_2$Se$_3$. 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 $\rho$ times $z$ over the whole supercell, where $\rho$ 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 $\alpha$-In$_2$Se$_3$ by DFT calculation.

Fig. S2 XPS spectrum of as-grown 2D In$_2$Se$_3$ 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$_2$Se$_3$. 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$_2$Se$_3$ 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 $\alpha$-In$_2$Se$_3$ devices for measuring OOP and IP PE loops. The thickness of nanoflake is $\sim$15 nm. The width of electrode is $\sim$3 µm. The channel length and width were $\sim$10 µm and $\sim$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 $\alpha$-In$_2$Se$_3$ nanoflakes transferred onto Nb:SrTiO$_3$. (a) The OOP PFM amplitude and phase hysteresis loop of a 7-nm thick $\alpha$-In$_2$Se$_3$. (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 $\alpha$-In$_2$Se 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$_2$Se$_3$ specimen with a thickness ranging from ~2 to 10 nm.

Fig. S10 The IP phase images of 2H-stacked α-In$_2$Se$_3$ nanoflakes in the different layers from 2 to 10. Scale bars: 40 nm.
Fig. S11 PFM studies of $\alpha$-In$_2$Se$_3$ nanoflakes transferred onto Pt/Ti/SiO$_2$/Si. IP PFM phase images of 5 (a) and 8 (b) layered 2H-stacked $\alpha$-In$_2$Se$_3$ 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 $\alpha$-In$_2$Se$_3$ 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 $\alpha$-In$_2$Se$_3$ based transistor ($V_{ds} = 2.5$ V) demonstrates the as-prepared $\alpha$-In$_2$Se$_3$ is a typical n-type semiconductor.

References