Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information for

Domain-structure-dependent electronic properties and carrier spatial distribution in two-dimensional α-In_2Se_3 ferroelectrics

Yanan Lu[1], Liqin Su[1], Linghui Fang[1], Qingyuan Luo[1], Meiying Gong[1], Dan Cao[2], Xiaoshuang Chen[3], Xiaowen Shi[4], Haibo Shu[1,]*

[1]College of Optical and Electronic Technology, China Jiliang University, Hangzhou 310018, People's Republic of China

[2]College of Science, China Jiliang University, Hangzhou 310018, People's Republic of China

[3]State Key Laboratory of Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Science, Shanghai 200083, People's Republic of China

[4]Hongzhiwei Technology (Shanghai) Co., Ltd., Shanghai 201206, People's Republic of China

[*]Corresponding author. E-mail: shuhaibo@cjlu.edu.cn, Phone: 86-0571-86875622

S1. Computational models

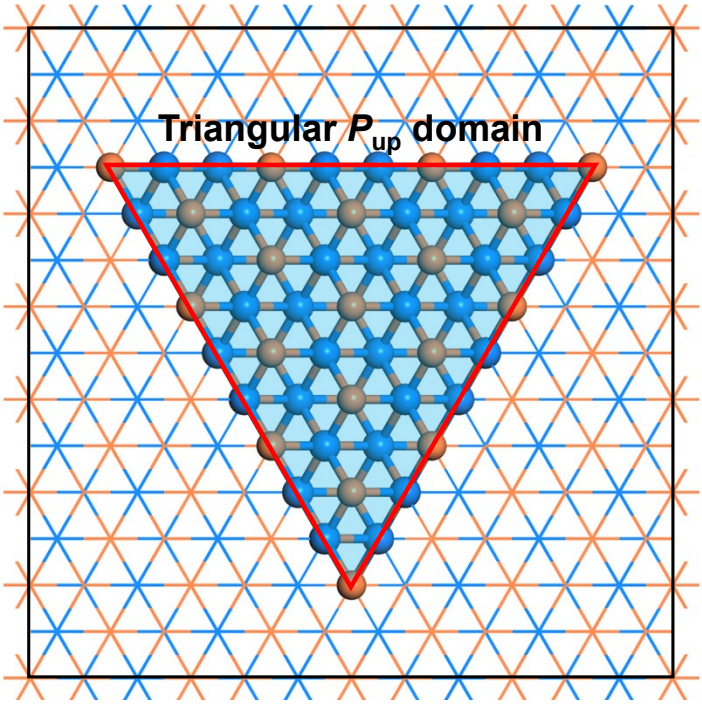

Fig. S1 Top view of $(4\sqrt{3}\times7)$ supercell atomic model for calculating the formation energies of domain boundaries in α-In_2Se_3 monolayer. Here a triangular domain in P_{up} state is embedded in a monolayer α-In_2Se_3 in P_{down} state. The red lines correspond to the domain boundaries. The size of the P_{up} domain is tuned by changing the length of domain boundaries. The blue and orange balls represent In and Se atoms, respectively.

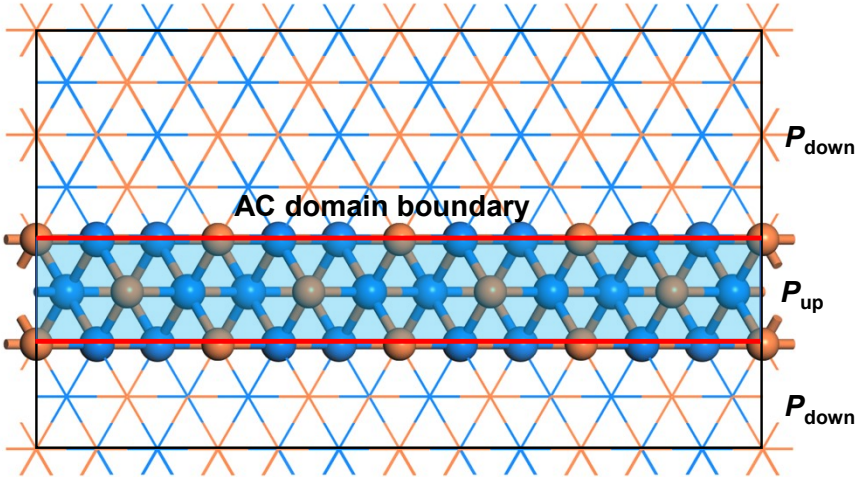

Fig. S2 Top view of $(4\sqrt{3}\times4)$ supercell model for investigating the boundary propagation during the domain expansion of α-In_2Se_3 monolayer. The red lines correspond to the AC domain boundaries.

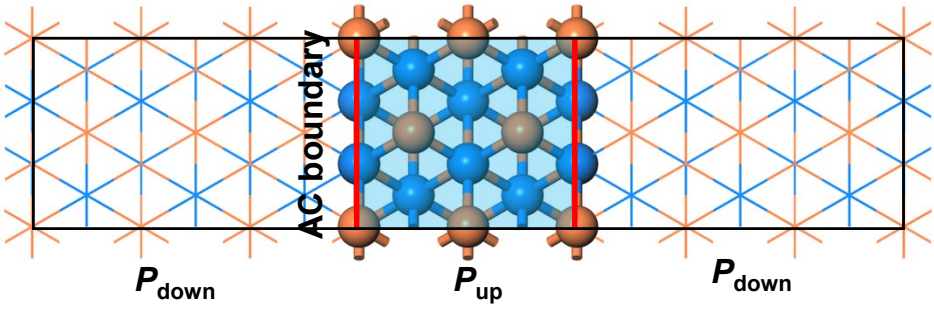

Fig. S3 Top view of $(\sqrt{3}\times 8)$ supercell model for calculating electronic structures of monolayer α-In_2Se_3 with different domain textures. The different domain textures can be obtained by expanding the domain area in P_{up} state.

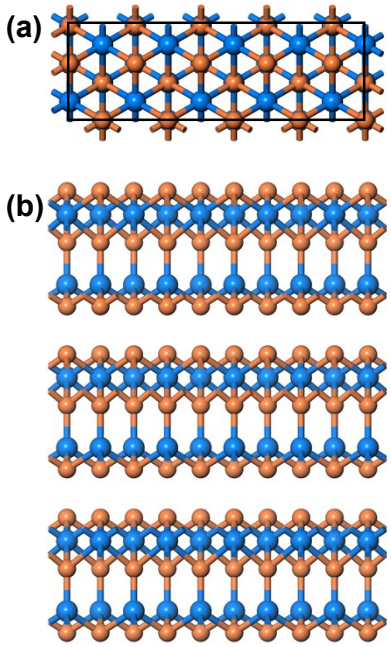

Fig. S4 (a) Top and (b) side views of supercell atomic model of a trilayer α-In_2Se_3. The black frame denotes the range of unit cell. The blue and orange balls denote In and Se atoms, respectively.

S2. Identification of Coulomb interactions between the P_{up} and P_{down} domains

Fig. S5 indicates the relative energy (ΔE) of monolayer α-In_2Se_3 domain textures with AC boundaries (see Fig. S3) as a function of switching domain ratio (R_{up}). It can be clearly seen that the formation of a P_{up} domain in the P_{down}-state α-In_2Se_3 monolayer induces a fast energy increase (~1.51 eV) due to the introduction of domain boundaries. However, there are few energy changes (< 0.1 eV) in the monolayer α-In_2Se_3 with the increase of R_{up}, suggesting that the expansion of domain boundaries does not bring the change of system energy. Therefore, the domain switching indued energy increment in monolayer α-In_2Se_3 mainly arises from the contribution of boundary formation energies, while the Coulomb interactions between the P_{up} and P_{down} domains barely contribute to the increase of system energy.

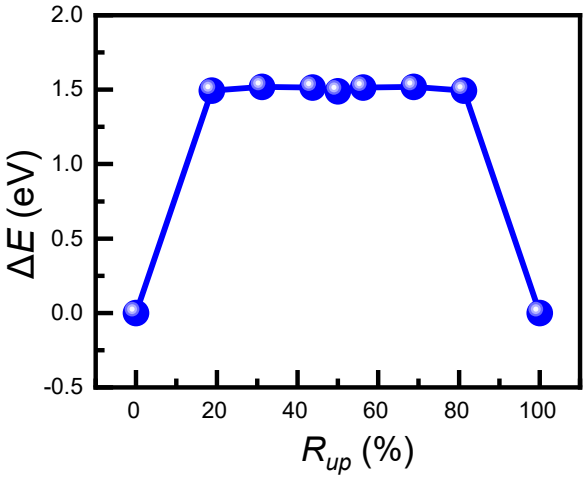

Fig. S5 The relative energy (ΔE) of monolayer α-In_2Se_3 domain textures as a function of switching domain ratio (R_{up}). The pristine α-In_2Se_3 monolayer in P_{down} state is used as the energy reference.

S3. The determination of formation energies of domain boundaries.

For a given triangular domain (Fig. S6a), its formation energy E_f is from the contribution of three vertices (γ_v) and three boundaries (γ_b) as follows,

$$E_f = 3\gamma_v + 3l\gamma_b = E_{domain} - E_{ref} \quad (1)$$

where E_{domain} and E_{ref} are the total energy of the monolayer α-In_2Se_3 with and without a switching triangular domain, respectively. Thus, the calculation of γ_b is transformed into a problem of eliminating the effect of the vertexes, which can be done by taking the energy difference between similar triangle models with different side lengths. As shown in Fig. S6a, by shrinking the length from l_1 to l_2, one has

$$\gamma_b = (E_f(l_1) - E_f(l_2))/3(l_1 - l_2) \quad (2)$$

Based on the calculated γ_b, γ_v can be obtained by eq. (1). Hence, the formation energy of triangular domain with arbitrary boundary length (l) can be determined. Fig. S6b shows the E_f of triangular domains with AC boundaries as a function of boundary length (l). The formation energy of triangular domains indicates a linear increase with increasing domain size.

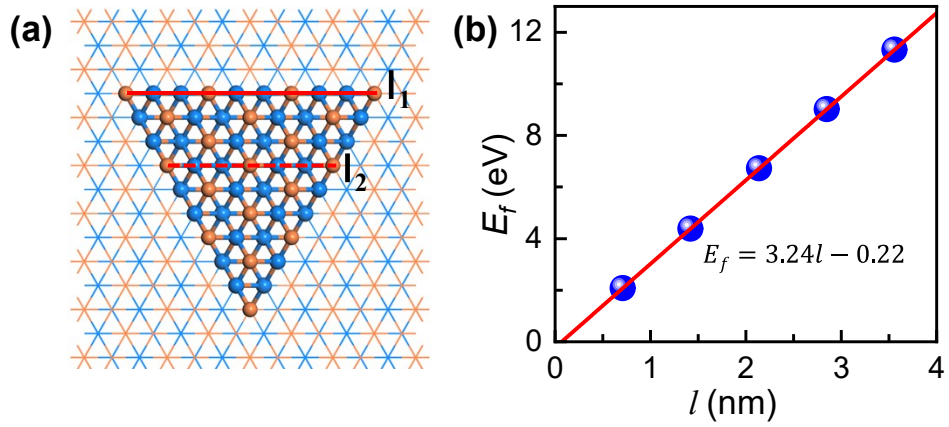

Fig. S6 The formation energies of domain boundaries in α-In_2Se_3 monolayer. (a) The calculated model for determining the boundary formation energies. The model is composed of a triangular P_{up} domain embedded in α-In_2Se_3 monolayer in P_{down} state. (b) The formation energy (E_f) of triangular domains with AC boundaries as a function of boundary length (l).

S4. Schematic of domain boundary propagation.

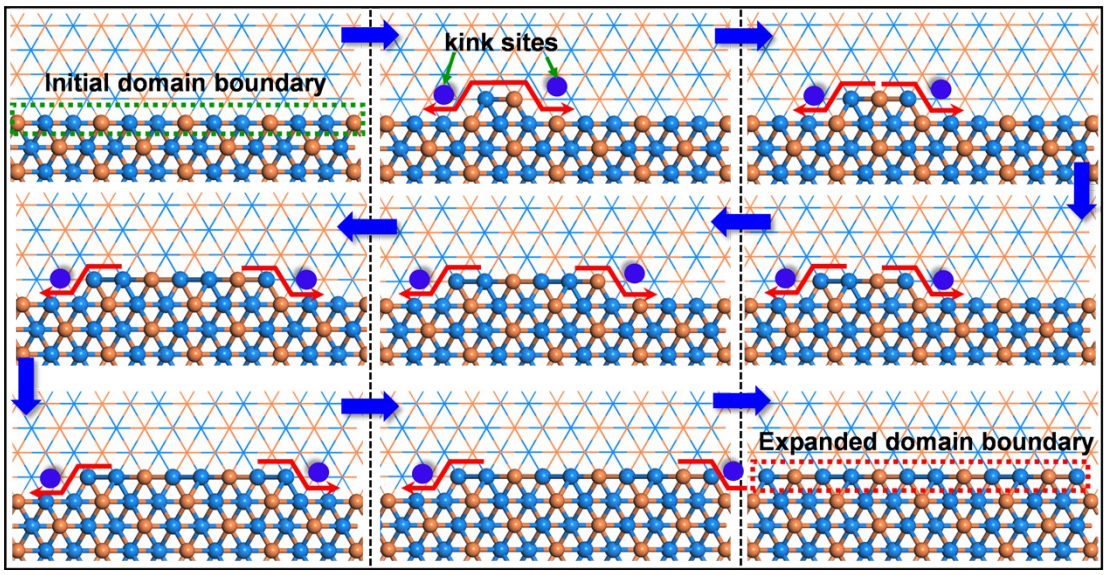

Fig. S7 Structural models of domain boundary expansion at a repeated cycle of polarization switching from P_{down} to P_{up} state in α-In_2Se_3 monolayer. The arrows indicate the domain boundary propagation pathway. In a sharp boundary between the P_{down} to P_{up} domains, the production of a new boundary step will lead to two kink sites followed by a repeatable cycle of boundary propagation.

S5. Schematic of polarization reversal in α-In_2Se_3 monolayer.

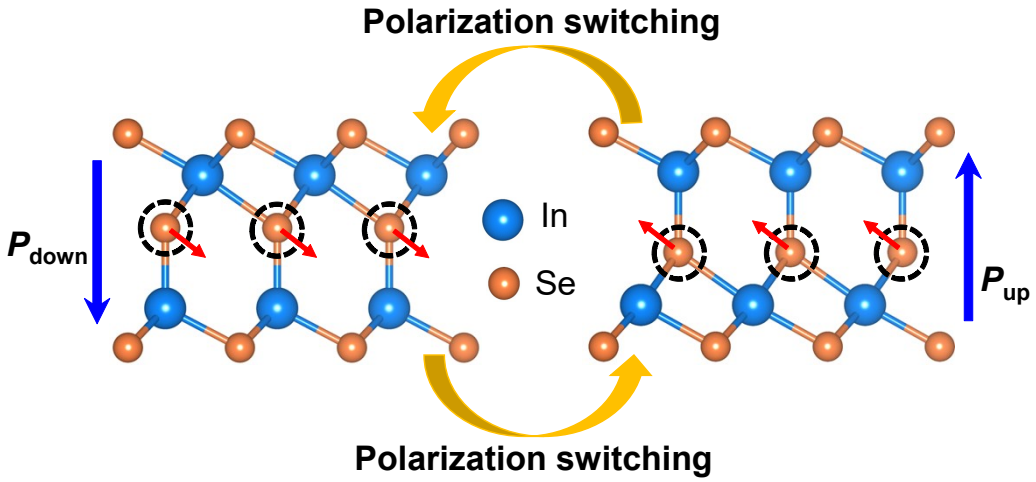

Fig. S8 Schematic polarization reversal of α-In_2Se_3 monolayer via the atomic movement. The arrows indicate the polarization direction.

S6. Electronic parameters in different α-In_2Se_3 domain textures.

Table S1 The dipole moments (μ), electrostatic potential difference(ΔV), band gap (E_g), and work function (W_F) of the α-In_2Se_3 monolayer at different R_{up} values.

R_{up} (%)	μ (Debye)	ΔV (eV)	E_g (eV)	W_F (eV)
0	8.13	1.39	1.43	6.62
18.75	5.33	0.92	1.62	6.41
31.25	3.21	0.58	1.73	6.31
43.75	1.05	0.18	1.83	6.18
50	0.02	0	1.85	6.10
56.25	-1.05	0.18	1.83	6.18
68.75	-3.21	0.58	1.73	6.31
81.25	-5.33	0.92	1.62	6.41
100	-8.13	1.39	1.43	6.62

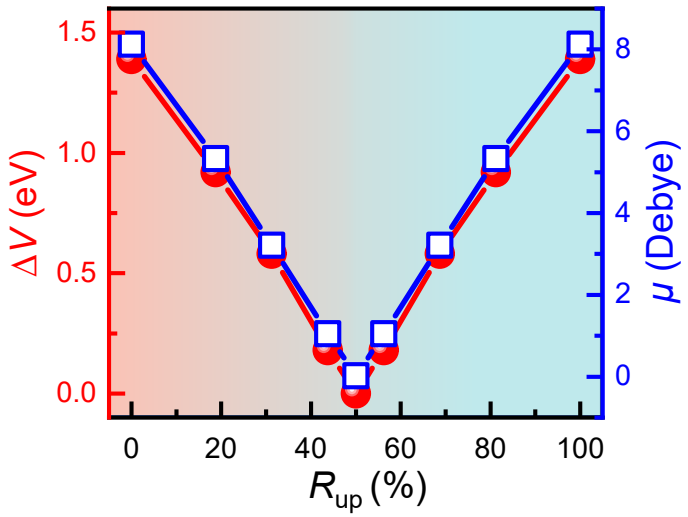

Fig. S9 The electrostatic potential difference ΔV (circles) and electric dipole moment μ (rectangles) of monolayer In_2Se_3 as a function of domain switching ratio (R_{up}).

S7. Domain-structure geometrics and stability of multilayer α-In_2Se_3.

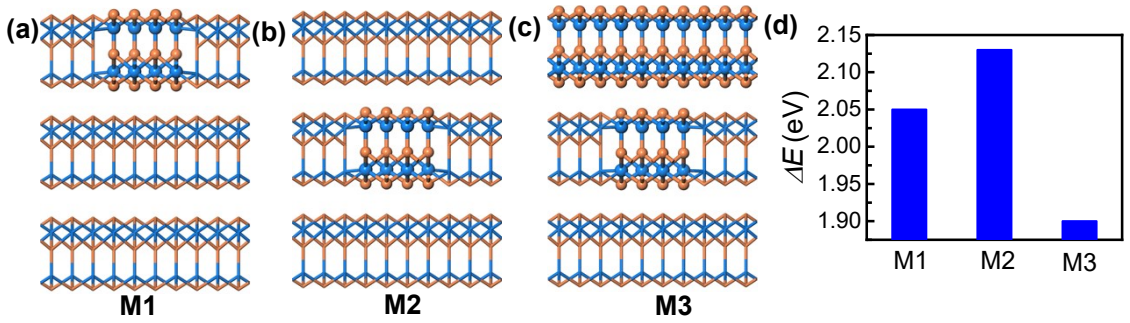

Fig. S10 Structural models and relative energy of trilayer α-In_2Se_3 with three different domain textures. (a) Trilayer α-In_2Se_3 with a P_{up} domain at the top layer (labeled by M1), (b) trilayer α-In_2Se_3 with a P_{up} domain at the center layer (labeled by M2), (c) The formation of a P_{up} domain near the P_{up} layer in trilayer α-In_2Se_3 (labeled by M3). (d) The relative energy (ΔE) of three domain textures (M1, M2, and M3). For M1 and M2, the relative energy is calculated by the energy difference between the domain texture and trilayer α-In_2Se_3 in P_{down} state. The relative energy of M3 is the energy difference between the M3 and trilayer α-In_2Se_3 with a top P_{up} layer.