Controlled switching of ferroelectric SnSe monolayers at room temperature

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Two-dimensional (2D) van der Waals ferroelectrics provide an unprecedented architectural freedom for the creation of artificial multiferroics and non-volatile electronic devices based on vertical and co-planar heterojunctions of 2D ferroic materials. Additionally, their non-centrosymmetric structures lead to a strong non-linear optical response, and also add functionalities to designer spintronic and valleytronic devices. Nevertheless, controlled electrical switching of in-plane polarization—a fundamental requirement for realizing in-plane ferroelectric non-volatile memories—has not yet been seen experimentally in any monolayer-thick 2D ferroelectric. Here we report the discovery of robust ferroelectricity with a critical temperature close to 400 K in SnSe monolayer plates, and the demonstration of controlled ferroelectric switching of their in-plane spontaneous polarization at room temperature using a scanning tunneling microscope (STM). The switching was achieved through creating, moving and eliminating 180° domain walls in the SnSe monolayer plates by applying appropriate bias voltage pulses to an STM tip. This study shows that STM is a powerful tool for detecting and manipulating the in-plane polarization in 2D ferroelectric monolayers, which is difficult to characterize by conventional approaches such as piezoresponse force microscopy, thus facilitating the hunt for other 2D ferroelectric monolayers with in-plane polarization with important technological applications.
As the research of ferroelectrics moves towards the 2D limit, the existence of ferroelectricity in monolayer (ML)-thick materials has been confirmed in both van der Waals MLs\textsuperscript{1,2} and epitaxial perovskites\textsuperscript{3}. Compared with traditional perovskite ferroelectric thin films, 2D ferroelectrics bring the freedom of fabricating functional van der Waals heterostructures without the restriction of lattice matching. Many layered ferroelectrics, such as CuInP\textsubscript{2}S\textsubscript{6}\textsuperscript{4}, SnTe\textsubscript{1,5-7}, In\textsubscript{2}Se\textsubscript{3}\textsuperscript{8-13}, WTe\textsubscript{2}\textsuperscript{14} and MoTe\textsubscript{2}\textsuperscript{2}, have been discovered in the past few years. Despite a recent demonstration of switching of the out-of-plane polarization in MoTe\textsubscript{2} MLs\textsuperscript{2}, the controlled electrical switching of in-plane polarization at the thickness of a single van der Waals ML has remained elusive. The out-of-plane polarization has been manipulated via piezoresponse force microscopy (PFM) or overlaid electrodes in several-layer thick van der Waals ferroelectrics\textsuperscript{4,8,10,12-14} and freestanding perovskite thin films\textsuperscript{27}, but the switching of in-plane polarization is a more complex process: for instance, ferroelectric SnTe ML, an isostructural cousin of the SnSe ML reported in this article, has been grown on graphene substrates in the recent past\textsuperscript{1,5-7}, but controlling its in-plane polarization has proven to be a formidable task. This is because conventional techniques employed to create in-plane electric fields in ferroelectric thin films are unsuitable for these MLs, as PFM lacks in-plane sensitivity at sub-nanometer film thicknesses and co-planar electrodes face short circuit problems on conductive graphene substrates. Previous studies have achieved only an uncontrolled switching through STM tip induced domain wall motion in SnTe MLs at 4.7 K\textsuperscript{1}. Overcoming these obstacles, we employed a variable temperature STM to controllably switch the in-plane polarization in SnSe MLs at room temperature, and to demonstrate its ferroelectric transition temperature to be as high as 380 ~ 400 K, the highest among the family of ferroelectric group-IV monochalcogenide MLs up to now. These results open the door to the potential fabrication of sub-nanometer-thick ultrathin memories, non-linear optic, spintronic and valleytronic devices that operate at room temperature.

We first establish the conformation of ultrathin SnSe nanoplates grown on epitaxial graphene prepared on 6H-SiC(0001) surfaces. Belonging to the noncentrosymmetric space group $Pnm2_1$, a SnSe ML contains two strongly bonded atomic layers separated by 2.8 Å. The lattice vectors $a_1$ and $a_2$ are parallel and perpendicular to the in-plane spontaneous polarization $P$, respectively. As seen in Fig. 1a, the edges of
rectangular SnSe ML plates occur along the \( <11> \) directions, with two edges hosting positive bound charges and the other two having negative bound charges. The SnSe plates display three relative crystalline orientations where \( a_1 \) (\( a_2 \)) aligns with the graphene’s zigzag (armchair) direction. Accordingly, their in-plane polarization points along one of the six directions shown in Fig. 1b given that a crystalline orientation allows two conformations with antiparallel polarizations. Such highly oriented growth, which is not seen for SnTe MLs on this substrate\(^1\),\(^6\), is further confirmed by reflection high energy electron diffraction (RHEED) patterns and large-scale \( dI/dV \) mapping images (Fig. S1 in Supplementary Information). By reproducing the moiré pattern between the SnSe MLs and graphene through a lattice simulation, we determine the lattice parameters for these SnSe MLs at room temperature to be \( a_1 = 4.35 \pm 0.02 \) Å and \( a_2 = 4.26 \pm 0.02 \) Å (Figs. S2-S4). The lattice parameter \( a_2 \) agrees with graphene’s periodicity along its armchair direction (\( \sqrt{3} \times 2.46 \) Å = 4.26 Å).

The spatially resolved \( dI/dV \) spectra in Fig. 1c—approximately proportional to the scanned surface’s local density of states (LDOS)—uncover an in-plane polarization by displaying band bending towards opposite directions at opposite edges of a single-domain SnSe ML plate, distinct from the band bending towards the same directions at opposite edges in non-polar semiconductors. The valence band maximum (VBM) lies at \(-0.44 \) eV and the conduction band minimum (CBM) at 1.69 eV at the center of this 50 nm wide SnSe ML plate, yielding an electronic band gap of 2.13 eV at 1.8 K. The CBM and VBM show +0.24 eV (upward) and \(-0.31 \) eV (downward) band bending at opposite edges in Fig. 1c. Fitting these band edge profiles with an exponential function \( V(x) = A \exp[-(x - x_0)/L_0] + V_0 \), we obtain decay lengths of \( L_0 = 4.22 \pm 0.23 \) nm for upward bending, and \( L_0 = 5.89 \pm 0.36 \) nm for downward bending (Fig. S5). Such an exponential decay is due to screening from the metallic graphene substrate. Without screening, the decay would take a much slower logarithmic form in a 2D ferroelectric with in-plane polarization, in analogy with the electric potential generated by charged wires.

Though still resolvable, band edges become less clear on \( dI/dV \) spectra acquired at room temperature (Fig. S6). In that case, and as seen in Figs. 1d and e, topographic and \( dI/dV \) mapping images still clearly display opposite charge accumulation at opposite edges resulting from band bending. The
tunneling current is roughly proportional to the sample’s LDOS integrated between \( eV_s \) and \( E_F \), where \( V_s \) is the sample bias voltage and \( E_F \) is the Fermi level set at 0 eV. The tip moves away from (closer to) the surface at a place with a higher (lower) integrated LDOS when the STM is operated in a constant current mode (keeping tunneling current \( I_t \) unchanged in the scan), generating a higher (lower) apparent height \( z \). Therefore, on an atomically flat surface, an edge with upward (downward) band bending shows a higher (lower) apparent height at a negative \( V_s \) close to VBM. At \( V_s = -0.2 \) V and \( I_t = 2 \) pA, the topographic image of the SnSe ML plate in Fig. 1d displays a contrast of 1.0 Å at opposite edges (\( \zup/\zdown = 1.2 \)), while the \( dI/dV \) image in Fig. 1e shows a contrast of 0.6 pS [\( (dI/dV)_{\up}\)/(dI/dV)_{\down} = 2.3 \)], both confirming an in-plane polarization parallel to \( a_1 \).

The highly oriented growth prohibits the existence of 90° domain walls that were predominantly seen in SnTe MLs\(^1\). Only 180° domain walls are observed in SnSe MLs, either in a straight (Fig. 1f) or zigzag shape (Fig. 1g). An atom-resolved image reveals identical lattice vectors in neighboring domains (Fig. S7) in agreement with the 180° domain orientation. The straight wall in Fig. 1f is 12° away from \( a_1 \), yielding a bound charge density \( \lambda_P = 0.42P \), where \( P \) is the in-plane polarization estimated to be \( 1.5 \times 10^{-10} \) C/m from our first principles calculations. The walls in Fig. 1g have domains joining “tail-to-tail” and the 34° zigzag angle leads to a bound charge density of \( \lambda_P = 0.58P \).

Now that the SnSe ML plates are characterized, we discuss the principal contribution of the present work: their controlled ferroelectric switching at room temperature by moving, creating and eliminating the 180° domain walls, achieved by applying bias voltage pulses with an STM tip situated at a lateral distance \( d_0 \) away from the SnSe plate as illustrated in Fig. 2a. The width of the uprising edge of these pulses is 0.14 ms (Fig. 2b), much longer than the relaxation time of the carriers in graphene\(^2\), thus the electric field induced by the pulse can be regarded as quasi-static. The pulse voltage \( V_p \) lasts for \( t_p = 50 \) ms, unless otherwise specified. In Figs. 2c-f, the switching process is demonstrated as a series of pulses were applied with the STM tip placed at \( d_0 = 20 \) nm away from a corner of the plate. There were two domains and a 180° domain wall across the plate at the onset; the domain with \( P \) parallel to \( E_\parallel \) expanded and the one with \( P \) antiparallel to \( E_\parallel \) shrunk as the first \( V_p = -5 \) V pulse was applied (Fig. 2c). The whole plate turned into a
single domain with $\mathbf{P}$ parallel to $\mathbf{E}_\parallel$ (Fig. 2d) after a second −5 V pulse took place. A new domain wall was created as a +8 V pulse was applied, and part of the polarization in this plate was switched to the opposite direction (Fig. 2e). Finally, another +8 V pulse set the whole plate into a single domain again but inverting $\mathbf{P}$ from its initial direction (Fig. 2f). The polarization of a SnSe ML plate can be repeatedly and controllably switched this way, and additional experiments are given in Fig. S8. In Supplementary Information, we also present a video to show back-and-forth domain wall motion by the applying bias voltage pulses of opposite signs with the STM tip staying at the same location.

Successful switching requires pulses to be applied on the graphene substrate and away from the SnSe ML plate, because the STM-tip-induced electric field has an out-of-plane component $E_z$ several orders of magnitude larger than its in-plane component $E_\parallel$ (Fig. 3a). Such a huge $E_z$ can lead to the electric breakdown when the tip is above a SnSe ML plate. For instance, assuming $V_P = 5$ V and a tip-sample distance of 5 Å, $E_z$ can easily reach $10^8$ V/cm beneath the STM tip.

Judging from Fig. 3b, which shows statistics of many single bias voltage pulse experiments, a pulse with shorter $d_0$ and larger $|V_P|$ has a higher probability of inducing domain wall motion. The uncertainty of the effect of a single pulse might be a result of the complicated shape of the STM tip and the environment of the SnSe ML plates—domain wall pinning could happen due to the defects, wrinkles or atomic steps on the substrate. In order to quantitatively determine the critical field of domain wall motion, $E_{\parallel,c}$, we carried out a series of experiments in which $|V_P|$ was gradually increased until domain wall motion was observed (see Fig. S8 for details). Comparing the experimental critical pulse voltages $|V_{P,c}|$ with the $E_\parallel$ obtained from numerical simulations in Fig. 3c (see also Fig. S9 for details of the simulations), we derived the corresponding critical fields for different $d_0$ in Fig. 3d. Our data suggests that for $d_0 \geq 30$ nm, $E_{\parallel,c}$ converges to $1.4 \pm 0.2 \times 10^5$ V/cm, which we consider to be the intrinsic critical field for domain wall motion. The $E_{\parallel,c}$ for shorter $d_0$ is higher, probably because of nonlinear electrostrictive effects induced by the very large $E_z$ at these distances.

We now determine the transition temperature $T_c$ above which the spontaneous polarization is suppressed. In Fig. 4, we used a variable temperature STM to study the temperature dependence of band
bending at the edges of the SnSe ML plate shown in Fig. 1d. The contrast of both apparent heights (Figs. 3a-f) and dI/dV (Figs. 3g-l) at opposite edges—both depending on the magnitude of band bending—decreases as the temperature is increased and becomes totally indistinguishable at 400 K (Figs. 4e,k,q). Band bending reappears as the temperature is decreased to 308 K, regaining the magnitudes registered before heating (compare Figs. 4a,g,m to Figs. 4f,l,r). This implies that the $T_c$ of SnSe MLs on graphene is between 380 K and 400 K, similar to that of bulk BaTiO$_3$ (396 K)$^{29}$, a well-known perovskite ferroelectric. For comparison, SnTe MLs on graphene substrates have a $T_c = 270$ K$^1$, a value below room temperature that may hinder practical applications.

In the end, despite the preferential orientation during growth discussed previously, SnSe ML plates can indeed be controllably moved by the STM tip on the graphene substrate without observable damage (Fig. S10), still implying a weak interaction between SnSe and the substrate. This makes the creation of heterostructures containing SnSe MLs by transferring and stacking techniques, or even by in situ scanning probe manipulations, likely to be feasible.

The discovery that highly oriented SnSe MLs on graphene are 2D ferroelectrics which can be controllably switched at room temperature brings predicted effects and device concepts based on group-IV monochalcogenide MLs—such as linearly-polarized-light-controlled valley selective excitations$^{16,21,23}$, shift current photovoltaics$^{24}$, intrinsic valley Hall effects$^{23}$, in-plane ferroelectric tunneling junctions$^{25,26}$, and nonlinear photocurrent switching devices$^{22}$—one step closer to reality. Additionally, we envision that the coupling between existing 2D ferromagnets and 2D ferroelectrics via vertical or horizontal heterojunctions may lead to an eventual deployment of layered artificial multiferroics.
Figure 1 | In-plane spontaneous polarization and domain walls in SnSe monolayer plates. a, Lattice structure of SnSe monolayer. The solid rectangle indicates a unit cell. Dashed lines indicate the preferred edge orientations of these plates. The signs of bound charges at opposite edges are labeled. b, Schematic diagram of three possible crystalline orientations of SnSe monolayers. The rhomboids and rectangles represent the unit cells of graphene and SnSe, respectively. Arrows in the rectangles indicate the directions of polarization allowed in this configuration. c, Spatially resolved $dI/dV$ spectra along the white dashed arrow across the SnSe monolayer plate shown in the inset, obtained at 1.8 K. Setpoints: $V_s = 3.0$ V, $I_t = 50$ pA for positive $V_s$; $V_s = −1.0$ V, $I_t = 50$ pA for negative $V_s$. The red dashed curves are exponential fittings of the band bending profiles. d,e, Room temperature topography (d) and simultaneously recorded $dI/dV$ (e) images of a SnSe monolayer plate. Setpoint: $V_s = −0.2$ V, $I_t = 2$ pA. f,g, $dI/dV$ images of SnSe monolayer plates with $180^\circ$ straight (f) and zigzag (g) domain walls. The domain walls are indicated by the white dashed lines. Setpoints: $V_s = −0.2$ V, $I_t = 2$ pA for f, $V_s = −0.35$ V, $I_t = 2$ pA for g.
Figure 2 | Controllable ferroelectric switching of SnSe monolayer plates. a, Schematic of ferroelectric switching achieved by applying a bias voltage pulse $V_p$ at a point on the graphene substrate close to a SnSe monolayer plate. The corner of SnSe closest to the STM tip was set as $d = 0$, and the upper surface of graphene was set as $z = 0$. b, Rising edges of the bias voltage pulses. Dashed lines indicate the onset and maximum values of the bias voltage. c-g, Consecutive $dI/dV$ images of a ferroelectric switching sequence in a SnSe monolayer plate. Setpoints: $V_t = -0.35$ V, $I_t = 2$ pA. The pulses were applied at the same point indicated in c. The widths of all the pulses were 50 ms. The directions of the in-plane components of tip-induced electric fields are indicated by the white arrows. All the data in this figure were collected at room temperature.
Figure 3 | Quantitative studies of the domain wall motion induced by bias voltage pulses. a, Simulated out-of-plane and in-plane electric fields along a horizontal line along the $d$ axis (see Fig. 2a) at the height of $z = 0.3$ nm. b, Statistics of a series of bias voltage pulse experiments with different $V_p$ and $d_0$. Each dot represents a single pulse applied. Those pulses that successfully moved a domain wall are shown in red, and those that did not induce domain wall motion are in blue. c, Simulated in-plane electric fields with $V_p$ fixed while varying $d_0$. d, The experimental $d_0$ dependence of the critical pulse voltages $|V_{p,c}|$ of domain wall motion (inset) and the corresponding $E_{d_0,c}$ at the closest corner of SnSe.
Figure 4 | Temperature dependence of ferroelectricity in a SnSe monolayer plate. a-f, Topography images of a SnSe monolayer plate at temperatures $T$ increasing from 310 K to 400 K from a to e, and decreasing to 308 K in f. Setpoints: $V_s = -0.2$ V, $I_t = 2$ pA. g-l, Simultaneously recorded $dI/dV$ images corresponding to a-f. m-r, Apparent height and $dI/dV$ profiles along the dashed arrows in a and g, extracted from a-f and g-l, respectively. s, Evolution of the difference of apparent height and $dI/dV$ between the two opposite edges with upward and downward band bending directions, extracted from m-q.
Methods

Sample preparation: SnSe monolayer plates were grown on graphene substrates via van der Waals molecular beam epitaxy in an ultra-high vacuum (UHV) chamber with a base pressure of $1 \times 10^{-10}$ mbar. Graphene substrates were prepared following a sequential direct current annealing procedure of nitrogen doped 6H-SiC(0001) (Si face). The substrate temperature was monitored by a high-precision infrared pyrometer. The 2 mm $\times$ 10 mm sized SiC substrate was first degassed at 500°C overnight, then annealed at 900°C in Si flux for 15 min to form a Si-rich $3 \times 3$ reconstruction. Finally, the substrate was annealed at 1400°C for 10 min to graphitize the surface. SnSe molecules were evaporated from a home-built thermal evaporator with an h-BN crucible containing 99.999% SnSe granules from Alfa Aesar. During growth, the SnSe evaporator was kept at ~450°C and the substrate temperature varied from 70°C to 220°C, depending on the specific plate shape desired. During growth, the substrate was heated by radiation from tungsten filaments, and temperature was read from a thermocouple. Higher substrate temperatures generate thicker plates with uniform thicknesses and straight edges, while plates grown at lower substrate temperatures are more irregular and have more ~6 Å high steps at their surfaces. Rectangular SnSe monolayer plates were grown in a two-step process: (i) by initially depositing irregularly shaped monolayer plates with a coverage lower than 0.05 monolayers at a substrate temperature of 70°C and (ii) a subsequent annealing up to 240°C for 1 h to turn the plates rectangular. If larger monolayer plates are desired, one can deposit SnSe again at the substrate temperature of 240°C, at which SnSe plates tend to grow horizontally.

Variable temperature scanning tunneling microscopy (VT-STM): As-grown samples were transferred into an Omicron VT-STM-XT system connected to the growth chamber without leaving the UHV environment. Mechanically sharpened Pt/Ir (80/20) alloy tips calibrated on an Au(111) standard sample were used for scanning. For the measurement of $\text{d}I/\text{d}V$ spectra and mappings, a sinusoidal modulation voltage of 30 mV with a 713 Hz frequency was added to the bias voltage. In the ferroelectric switching experiments, the tip was first stabilized at the parameters for scanning (typically $-0.2 \sim -0.4$ V, 2 pA), and then the feedback look was turned off when a pulse voltage (typically $\pm 3 \sim \pm 8$ V) was applied. The feedback loop was turned on immediately at the end of a pulse. A Lakeshore 335 temperature controller was used for
the variable temperature experiments. The temperature ramping speed was limited to <5°C/min, and the STM kept scanning during the ramping process in order to track the thermal drift of the sample. At each temperature setpoint, the temperature was stabilized for at least 30 min to reduce thermal drift. For collecting the $dI/dV$ spectra at room temperature, the bias voltage was scanned both forward and backward to compensate the drifting of tunneling junction width. Acquiring each spectrum took only 3~4 seconds. 20 spectra were averaged at each point in order to reduce the noise.

**Low temperature scanning tunneling microscopy (LT-STM):** Low-temperature measurements were performed using a cryostat (Oxford Instruments) equipped with an UHV insert hosting the STM head (Sigma Surface Science). A steady state temperature of 1.8 K is achieved by continuously pumping the $^4$He cooling circuit. Samples were transferred from the MBE system to the LT-STM using a vacuum suitcase with a pressure in the $10^{-10}$ mbar range, thus always preserving UHV conditions. STM data were obtained using electrochemically etched W tips. Before measurements, the tips were conditioned on an Ag(111) single crystal. $dI/dV$ spectra were acquired by a lock-in technique, using a bias voltage sinusoidal modulation of 30 mV at a frequency of 736 Hz. To avoid any drift, line spectra across SnSe monolayer plates were taken after scanning the very same area for several hours. Each line consists of 200 points and was measured in approximately 6 hours. Positive and negative energy ranges were acquired separately.

**Ab initio calculations:** *Ab initio* calculations with the VASP code$^{30,31}$ that employ the self-consistent van der Waals exchange correlation functional as implemented by Hamada were carried out. In these calculations, 17 unit cells of the SnSe monolayer were almost commensurate with 30 rectangular graphitic cells (each containing 8 atoms) down to less than 0.5% strain. In addition, periodic 180° domains 15 nm wide were created using methods similar to those employed in References 15, 18 and 32, by the vertical stacking of 35 rectangular unit cells with polarization parallel to lattice vector $a_1$, and 35 additional unit cells with polarization antiparallel to $a_1$. The antiparallel unit cells were displaced horizontally until a minimum energy was found, and a subsequent structural optimization employing 25 k-points along the horizontal direction until forces were smaller than 0.01 eV/Å. The projected density of states was produced
employing 100 k-points along the horizontal direction, and spin orbit coupling was included in these calculations.

**Numerical simulations of electric field:** The numerical simulations were performed with COMSOL software. The electric field was set as static in the simulations. The diagram and parameters of the model and the calculated results are included in Fig. S9 of Supplementary Information.

**Data availability**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Code availability**

The code that support the findings of this study are available from the corresponding author upon reasonable request.

**Acknowledgements**

We thank Z. K. Liu for providing the SiC substrates, and J. D. Villanova, S. P. Poudel and Y. Zhuang for technical assistance. K.C., F.K., J.-R.J., P.S. and S.S.P.P. were supported by Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – Project number PA 1812/2-1. B.J.M. and S.B.L. were funded by an Early Career Grant from the U.S. Department of Energy, Office of Basic Energy Sciences (Award DE-SC0016139). Calculations were performed at University of Arkansas' Trestles, funded by the U.S. National Science Foundation (Grants 0722625, 0959124, 0963249, and 0918970), a grant from the Arkansas Economic Development Commission, and the Office of the Vice Provost for Research and Innovation, and at Cori at NERSC, a U.S. DOE Office of Science User Facility operated under Contract No. DE-AC02-05CH11231.
Author contributions
K.C. and S.S.P.P. designed the experiments. K.C. and J.-R.J. prepared the samples and performed the VT-STM experiments. F.K. and P.S. conducted the LT-STM experiments. B.J.M. and S.B.-L. carried out the ab initio calculations. J.-L.Z. performed the numerical simulations of electric fields. K.C., P.S., S.B.-L. and S.S.P.P. wrote the manuscript. All coauthors read and commented on the manuscript.

Additional information
Supplementary Information containing Figures S1-S10 is available at…
Supplementary Information also contains a video showing the consecutive motion of a domain wall induced by a series of pulses.

Competing financial interests
The authors declare no competing financial interests.

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