Electronic Supplementary Information

Evidence of Thickness-dependent Surface Induced Ferroelectricity in Few-layer Germanium Sulfide obtained via Scanning Tunneling Spectroscopy

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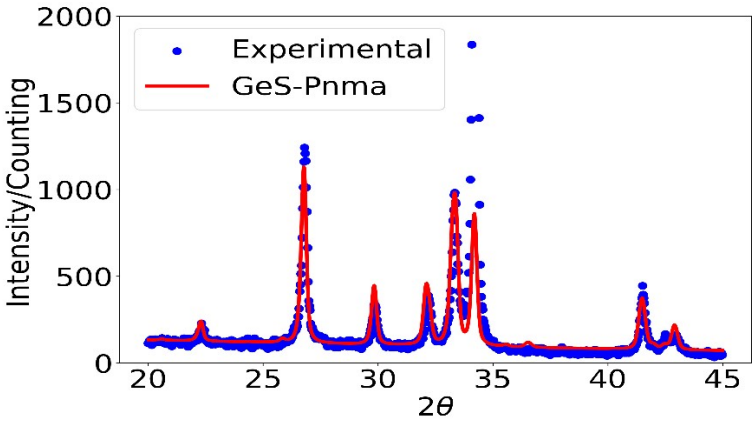


Figure S1: X-ray power diffraction pattern of our GeS sample. The blue dots are the experimental data and the red line is the fit using MAUD software for GeS Pnma phase.

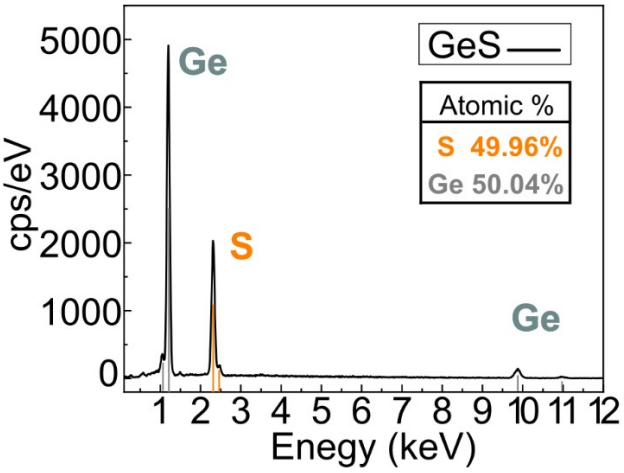


Figure S2: Energy dispersive spectroscopy of our GeS crystal.

Element	Region 1 (%)	Region 2 (%)	Region 3 (%)	Region 4 (%)	Region 5 (%)	Region 6 (%)
S	48.88	49.18	49.40	49.46	51.88	48.32
Ge	50.95	49.49	50.18	50.54	49.04	49.68

Table 1. Atomic ratio of Germanium and Sulfur at different regions of the crystal, as obtained by Energy Dispersive Spectroscopy.

Structure	Phase	hkl	Position (2^{θ})	Relative Intensity	Structure Factor
GeS	Pnma	002	14.1	9.4	20.7
GeS	Pnma	110	26.65	35.5	78.8
GeS	Pnma	111	27.74	40.4	87
GeS	Pnma	004	28.52	100	139.5
GeS	Pnma	021	34.56	15	68.1
HOPG	P63mc	002	22.15	100	17.3
HOPG	P63mc	004	45.19	7.2	10
Al	Fm-3m	111	31.86	35.8	100
Al	Fm-3m	200	37.02	49	34

Table 2. X-Ray experimental peaks relating the information of structure, phase, HKL indices, relative intensity and structure factor for GeS, HOPG and Aluminum. The relative intensities and structure factors for each structure were calculated individually.

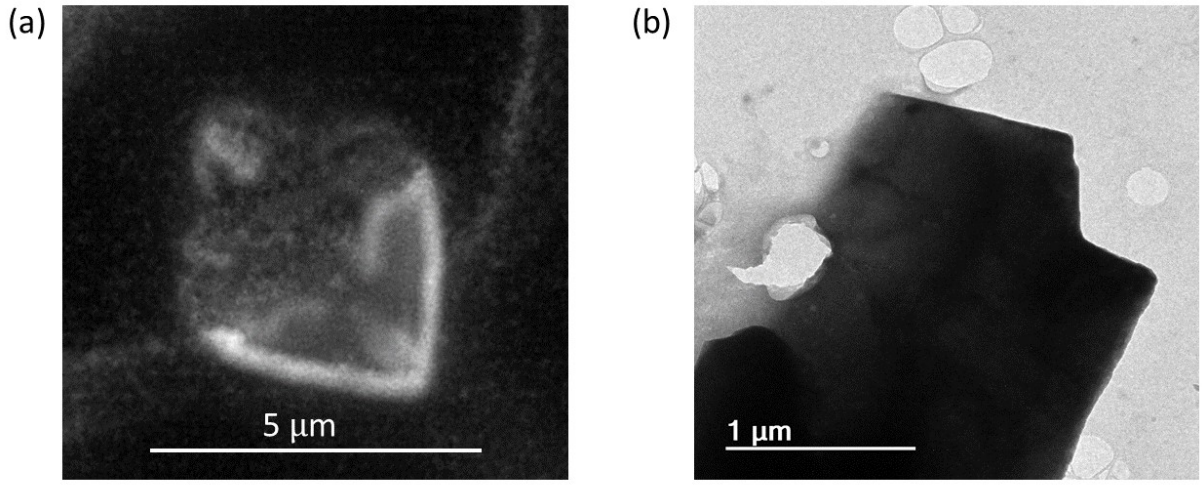


Figure S3: (a) Optical image of a GeS flake. (b) The low magnification image of the edge of a small GeS flake film fixed onto the carbon film on TEM grid.

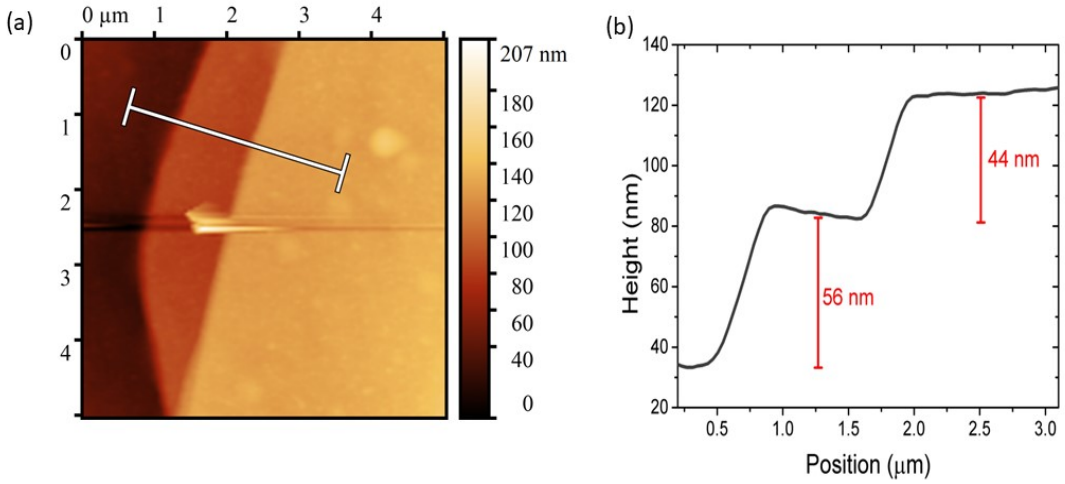


Figure S4: (a) STM image of stacked GeS flakes, with the parameters area = 5 µm x 5 µm, I_t= 800pA and V_{tip}=- -2V. (b) Flake profile along the white line in (a) showing the height of the stacked flakes.

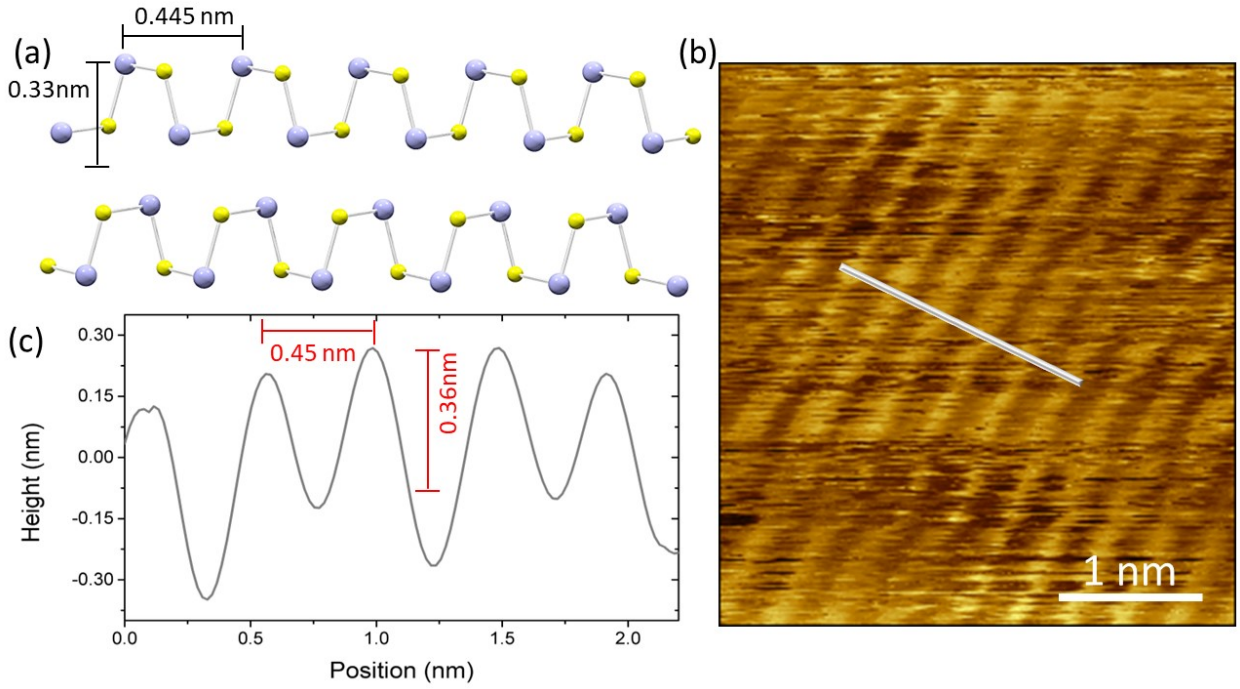


Figure S5: (a) Atomic structure of the GeS Pnma phase. (b) STM atomic resolution of our GeS sample. STM image with sensitivity to atomic stripes was taken using $I_T = 500pA$ and $V = 2V$, with a measurement field of view of 4nm x 4nm. (c) Atomic topography profile obtained in (b).

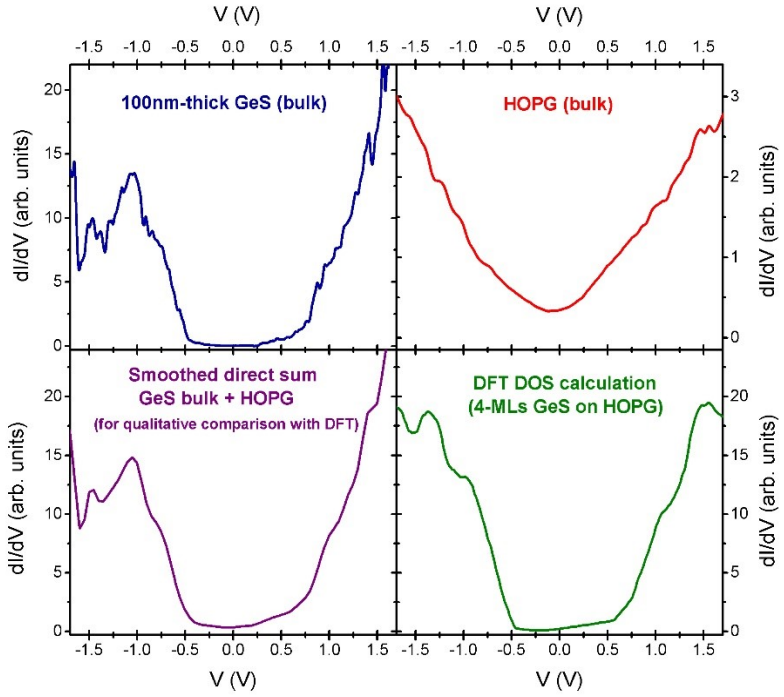
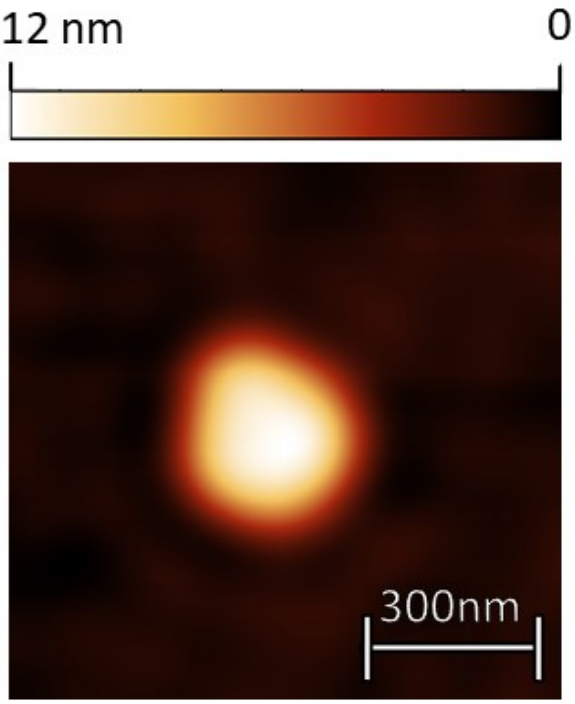


Figure S6: Comparison of scanning tunneling spectroscopy measurements of GeS (upper left), HOPG (upper right) and GeS flake on HOPG with a calculated density of states of 4 monolayers of GeS on HOPG (lower right).



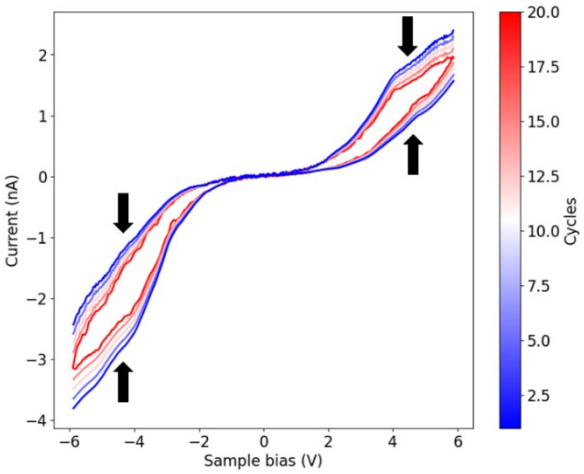


Figure S8: Germanium sulfide I-V curves for different cycles in the same spot at 2-nm thicker nanoflake. The color map is related to the number of cycles.

Figure S7: AFM image of the GeS nanoflake with 12nm height.

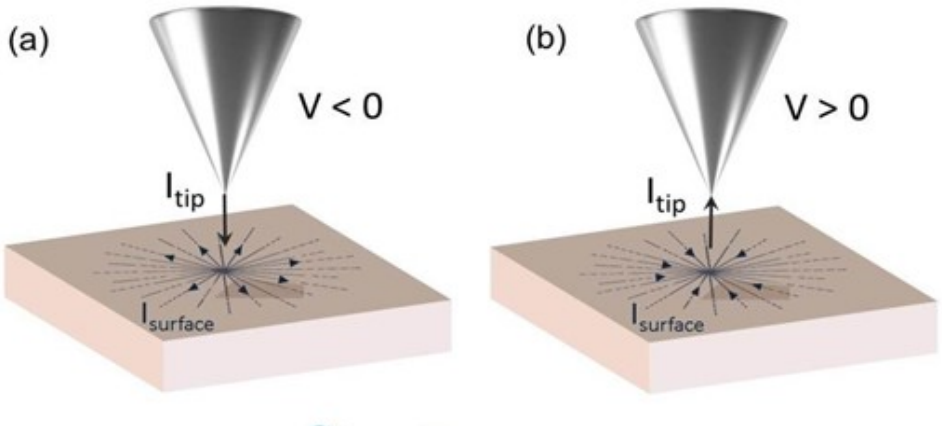


Figure S9: A schematic representation of the experiment, the resulting tunnelling and surface currents are shown in panels (a) for negative tip bias and (b) positive bias.