Supporting Information for:

Layer-dependent Electronic Structure of Atomically Resolved Two-Dimensional Gallium Selenide Telluride

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Methods

1. Sample preparation. The bulk crystal of $GaSe_{0.5}Te_{0.5}$ was purchased from 2D Semiconductors. For STEM imaging and EELS, the crystal was mechanically exfoliated onto polydimethylsiloxane (PDMS) films and transferred onto silicon nitride TEM grids. Monolayers were obtained through both exfoliation and beam-induced removal of layers, and they were confirmed by creating a hole in the crystal using the electron beam. For SHG measurements, $GaSe_{0.5}Te_{0.5}$ samples were exfoliated on a silicon substrate with a 90 nm SiO_2 layer in a nitrogen atmosphere and were measured in vacuum to limit air exposure.

2. Annular Dark Field Scanning Transmission Electron Microscopy (ADF-STEM) and electron energy loss spectroscopy (EELS). We used an aberration-corrected FEI Titan3 (60−300) equipped with a GIF Quantum spectrometer at 80 kV for ADF-STEM imaging and EELS measurements. For image acquisition, we used a camera length of 115 mm and a beam current of 30-50 pA. EELS measurements were performed in the TEM mode from a larger area. DualEELS mode was used for collecting the EELS data using a dispersion of 0.01 eV/channel and a 2.5 mm aperture. The energy resolution was calculated to be 0.1 eV, extracted from full-width at half maximum (FWHM) of the zero-loss peak.

3. Simulation of ADF-STEM images. Simulations of the ADF-STEM images were performed using the MacTempas software. Conditions the same as the experiment were used for the image simulations, including the probe semi-angle of 28.9 mrad and semi-collection angles of 42-244 mrad.

4. First principles calculations. We perform density functional theory (DFT) calculations with the ABINIT software[1] to determine the geometry and electronic structure of the few-layers Ga2SeTe alloy. We use a PBE exchange-correlation functional with Van der Waals corrections including 3-body corrections[2]. The fully relativistic pseudopotentials (including spin-orbit coupling) are generated using the ONCVPSP software[3] with valence electrons composed of $3d^{10}4s^{2}3p^{1}$ for Ga, $3d^{10}4s^{2}3p^{4}$ for Se, and $4d^{10}5s^{2}4p^{4}$ for Te. We use a kinetic energy cutoff of 55 Ha and the equivalent of a 12_12_1 k-point grid for a hexagonal unit cell. The cell parameters are optimized to reach a stress tensor below 2×10^{-3} eV/Å^3 and the atomic coordinates are relaxed to reach forces below 0.01 eV/Å.

5. Polarization-dependent second harmonic spectroscopy. A regenerative amplifier (Light Conversion PHAROS) produced femtosecond pulses (repetition rate of 150 kHz and duration of ~300 fs) that were used to pump an optical parametric amplifier (Light Conversion TOPAS) to generate pulses at 800 nm. This beam was focused to a spot size of ~ 5 um using an objective lens and the power was set well below the damage threshold (~35 uW). The second harmonic signal at 400 nm was collected using the same objective and analyzed with a monochrometer and a liquid-nitrogen-cooled charge coupled device. A polarizer was used to set the linear polarization of the 800 nm beam, and a half wave plate was used to rotate the plane of polarization relative to the samples. The component of the second harmonic signal that was parallel to the input polarization was measured using a second polarizer in front of the spectrometer.

Supporting Figures

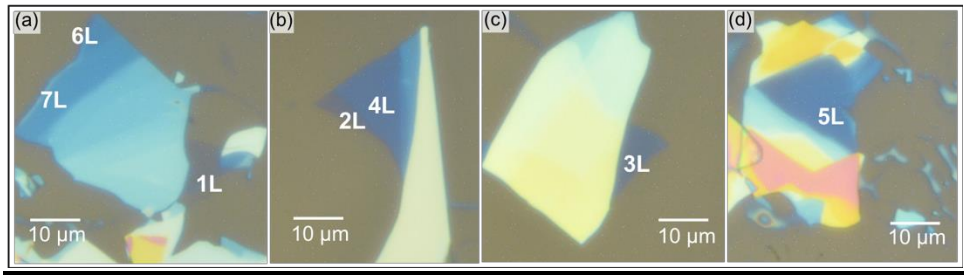

Figure S1. Optical images of the $GaSe_{0.5}Te_{0.5}$ flakes with different layer numbers: (a) 1L, 6L, and 7L, (b) 2L and 4L, (c) 3L, and (d) 5L. The samples were exfoliated directly onto a silicon substrate with a 90 nm SiO_2 layer in a nitrogen atmosphere.

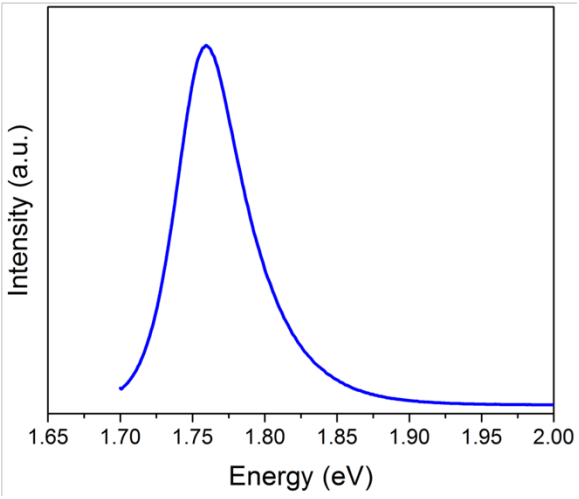

Figure S2. Photoluminescence spectra acquired from a thick $GaSe_{0.5}Te_{0.5}$ crystal.

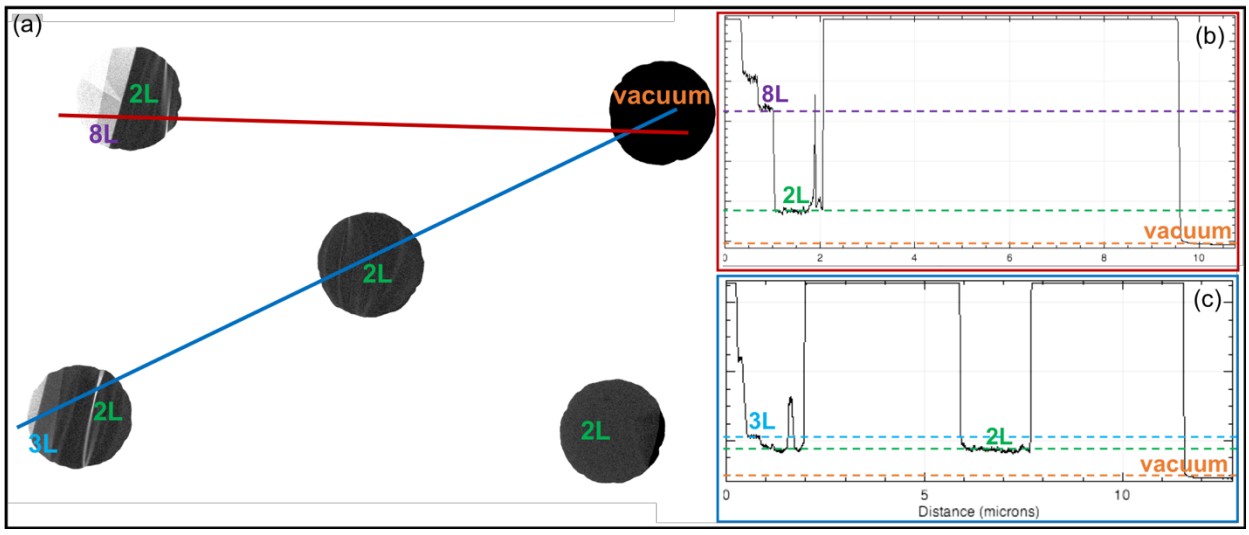

Figure S3. (a) Low-magnification ADF-STEM image of a $GaSe_{0.5}Te_{0.5}$ crystal with the bilayer, trilayer and eight-layer regions used for the EELS measurements. Intensity profiles along (b) red and (c) blue lines. The layer number of the different flakes in the STEM image were determined by looking at their intensity variation with respect to the intensity of a hole as the reference.

References

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