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Supporting Information

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Revealing the Preferred Interlayer Orientations and Stackings of Two-Dimensional Bilayer Gallium Selenide Crystals**

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Supporting Information

Experimental

Synthesis of bulk GaSe crystals. Ga_2Se_3 (99.99%, Alfa Aesar) and Ga (99.99%, Alfa Aesar) were mixed at a molar ratio of 1:1 and then sealed in an evacuated quartz tube under $<10^{-3}$ Torr of argon. The mixture was heated to 950 °C (from 25 to 700 °C in 35 min and 700 to 950 °C in 25 min) and maintained at temperature for 1 h. After heating, the system was cooled down first to 850 °C in 2 h and then naturally to room temperature.

Growth of 2D GaSe crystals. The synthesis of 2D GaSe was carried out in a tube furnace system equipped with a 1" quartz tube. Bulk GaSe crystals and Ga_2Se_3 powder were mixed together (GaSe:Ga_2Se_3 molar ratio ~50/1), and were used as source materials. SiO_2 (~300 nm)/Si pieces (1×1 cm^2) were cleaned with acetone, isopropyl alcohol (IPA), and DI water, and used as growth substrates. In a typical run, ~60 mg of source powder and a piece of SiO_2 (~300 nm)/Si substrate were loaded on a quartz boat, and subsequently inserted into the furnace. The source was located at the center of the furnace, with the substrate located ~8−10 cm downstream. After evacuating the tube to ~5 $\times 10^{-3}$ Torr, the reaction was conducted at 750 °C (with a ramping rate of 20 °C/min) for 5 min at a pressure of 30 Torr and an argon carrier gas flow rate of 60 sccm. The vapor-phase reactants were transported by the flowing argon gas to the growth region, in which the temperature was ~710−720 °C, thereby feeding the growth of the 2D GaSe crystals. After growth, the furnace was cooled naturally to room temperature.

Material characterization. The morphologies of the 2D GaSe crystals were characterized using scanning electron microscopy (SEM, Zeiss Merlin SEM) and atomic force microscopy (AFM, Bruker Dimension Icon AFM). The composition was analyzed using energy-dispersive x-ray spectroscopy (EDS) within the SEM.

The crystal structures of the 2D GaSe were investigated using transmission electron microscopy (TEM), dark-field TEM (DF-TEM), and aberration-corrected scanning transmission electron microscopy (STEM). TEM imaging and diffraction were conducted using an FEI Technai T12 at 100 kV at low dose densities, and no detectable damage was observed during imaging. Acquisition times for DF-TEM images (both displaced-aperture and centered DF-TEM) were 2 s per frame. The STEM images were obtained using an aberration-corrected Nion

UltraSTEM^{TM} 100 operating at 100 kV, using a half-angle range of the annular dark field detector with angles ranging from 86 to 200 mrad. The samples for TEM and STEM analysis were grown directly on amorphous silicon films (5 nm in thickness) supported by silicon TEM grid using the same growth process as described above.

Raman measurements were performed using cw excitation at 532 nm under a microscope (Jobin Yvon Horiba, T64000) using a long distance objective (100x, N/A = 0.8). The spot size on the sample was ~ 1 μm.

Theoretical modeling. We performed electronic structure calculations using a highly accurate, all-electron first-principles quantum mechanical calculation code with numerical atom-centered orbitals (NAO) as basis set (FHI-aims[1]). The exchange-correlation potential of the Perdew-Burke-Ernzerhof (PBE) version of the generalized-gradient approximation (GGA)[2] was used. In addition, non-empirical vdW corrections based on the PBE charge densities[3] were performed to capture the long-range dispersion interactions, which are missing in the conventional exchange-correlation functionals. We adopted experimental lattice parameters for ε and β bulk to construct corresponding bilayer island configurations.

We modeled bilayer configurations consisting of equilateral triangle GaSe flakes of sizes ranging from edge lengths of two Ga-Se units up to ~6 nm long on top of the triangular bottom layer of ~8 nm edge length. In order to efficiently describe the energies (interlayer interactions) of the structures consisting of over ~1000 atoms, our energy consists of only the key components, vdW energy and Coulomb energy. The coefficients for the pairwise vdW potential are extracted from the PBE+vdW potential.[44] In addition we take into account the ionic characters of the crystal and imposed ±1 e charges to each Ga and Se. We found that the Coulomb interactions between the layers also played an important role. Our theoretical approach enables us to effectively calculate many configurations of large-scale systems, where DFT approach is not feasible because of its high computational cost.

ADF image simulation. Simulated ADF image was obtained using the QSTEM package with similar experimental imaging conditions (100 kV, Cs = 0.21 μm, C5 = 0.24 mm, detector half-angle = 58-200 mrad, convergence semi-angle of incident probe =30 mrad).

[1] V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter, M. Scheffler, Comput. Phys. Comm. 2009, 180, 2175.

[2] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 1996, 77, 3865.

[3] A. Tkatchenko, M. Scheffler, Phys. Rev. Lett. 2009, 102, 073005.

Supporting Figures

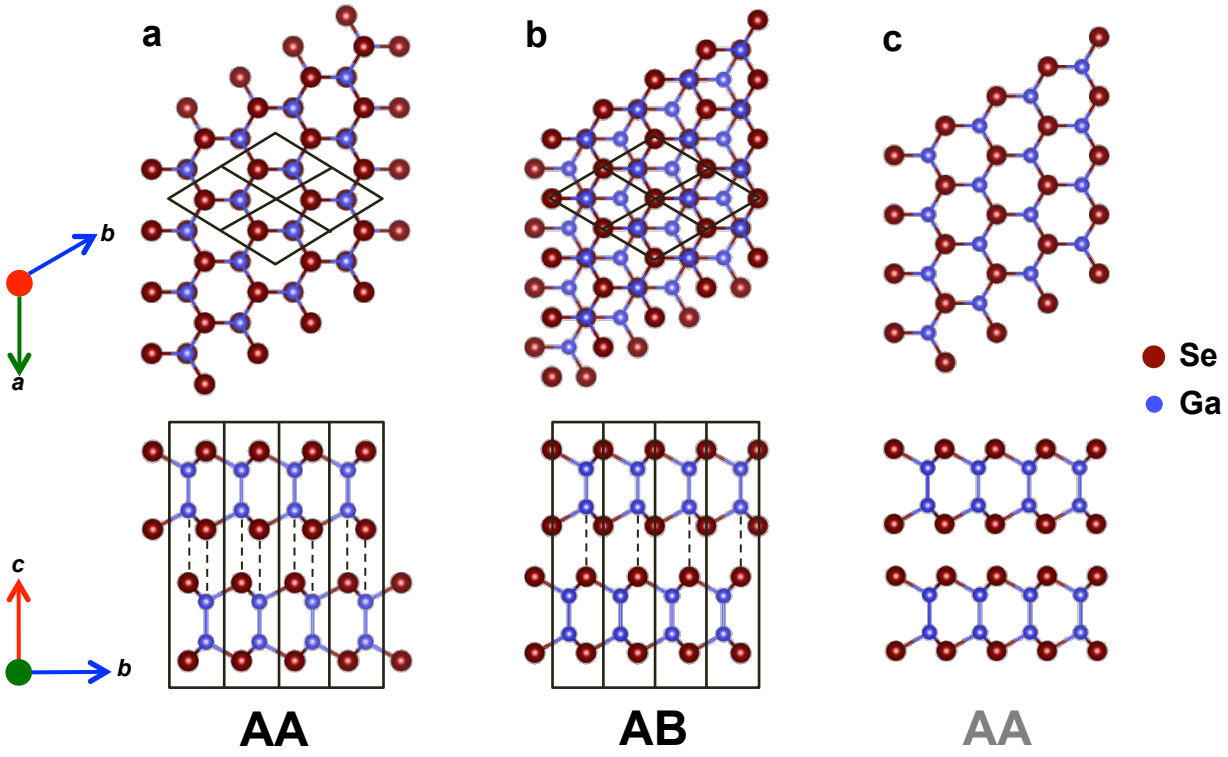

Figure S1. Schematic illustrations of three possible stacking modes of bilayer GaSe. (**a**) AA' stacking, corresponding to the bulk β-polytype. (**b**) AB stacking, corresponding to the bulk ε-polytype. (**c**) AA stacking, which does not exist in bulk GaSe.

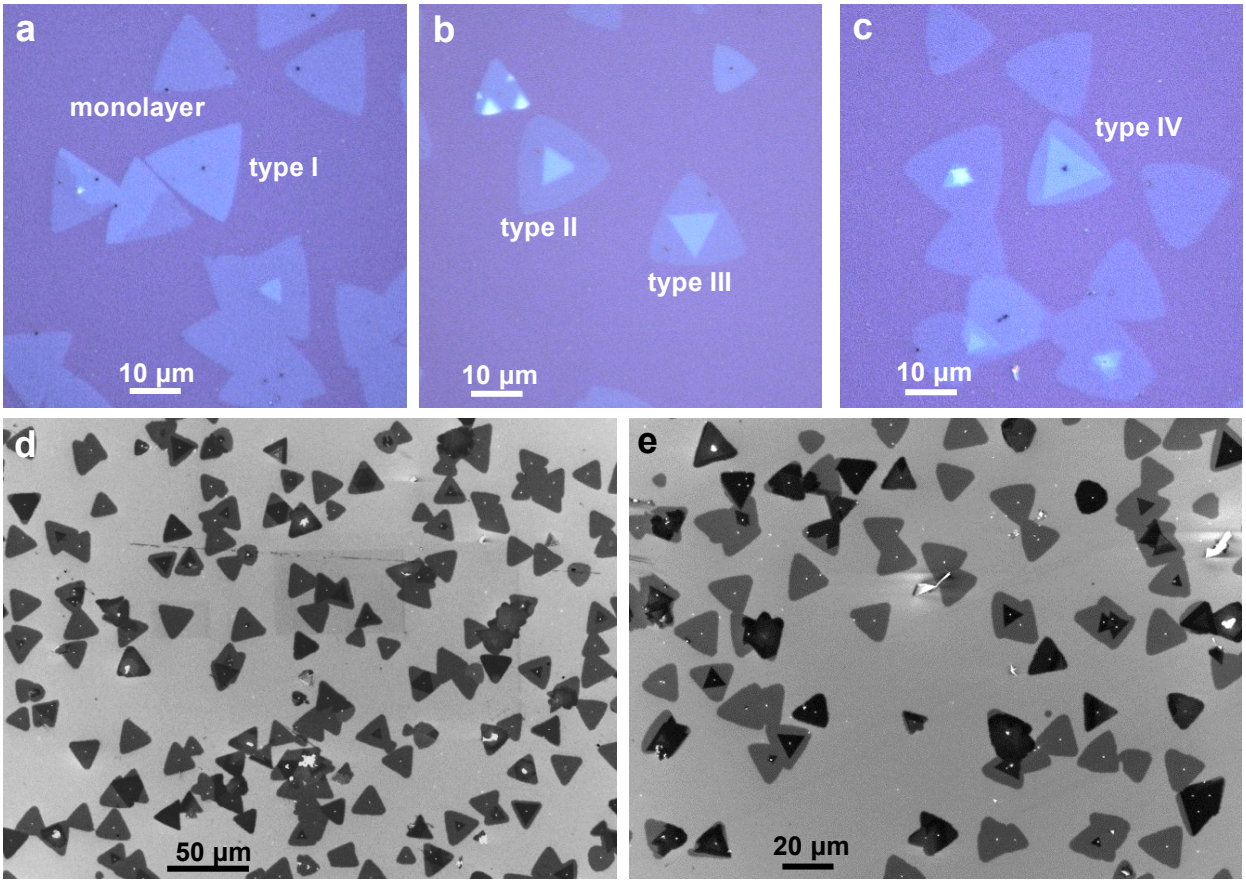

Figure S2. Morphologies of 2D GaSe crystals. (**a**−**c**) Optical micrographs of 2D GaSe crystals, showing monolayer crystals, type I, II, III and IV crystals. (**d**−**e**) Typical low magnification SEM images of triangular 2D GaSe containing both monolayer and multi-layer crystals with different stacking modes.

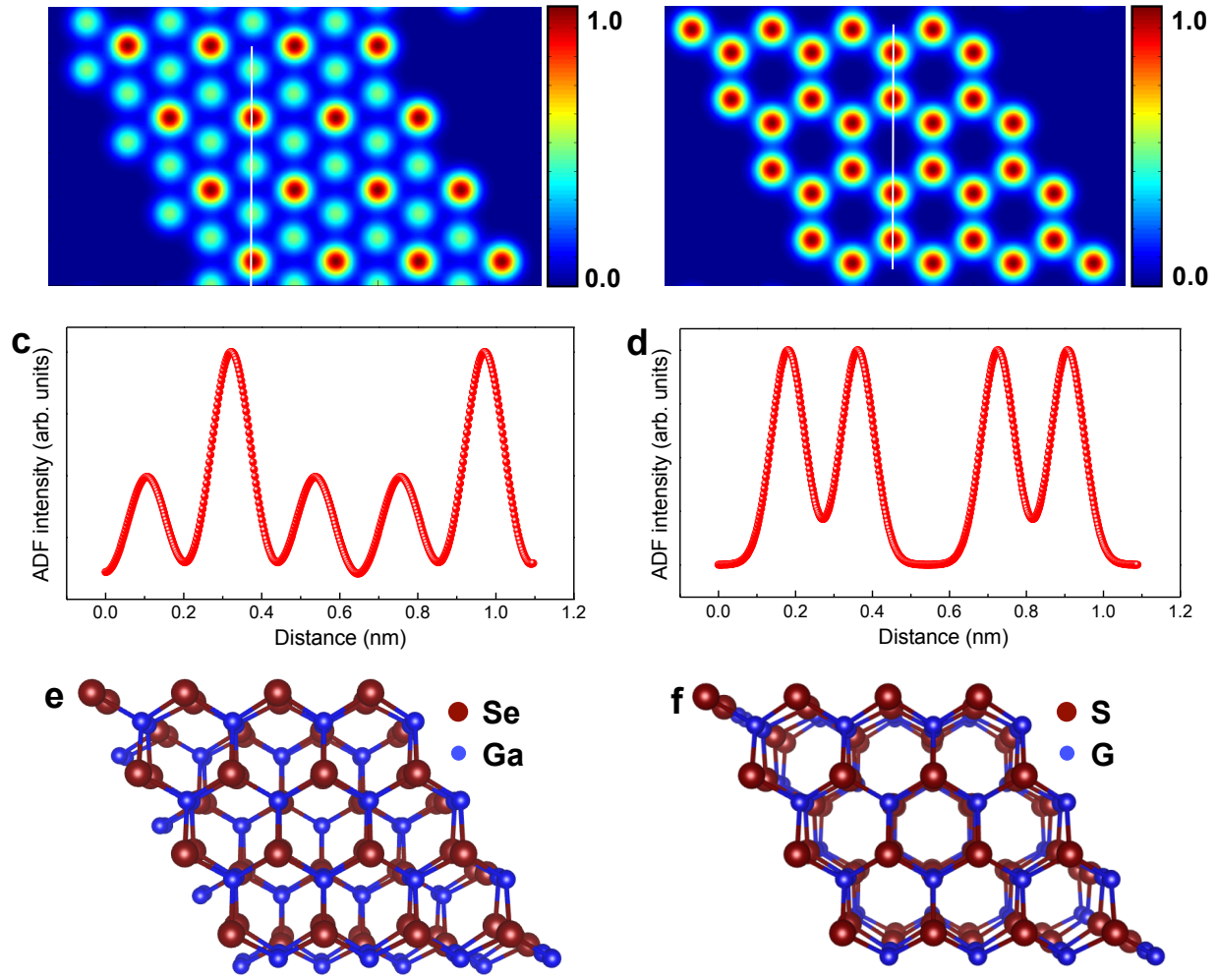

Figure S3. Modeled structure and simulated ADF images of bilayer GaSe with AB (ε) and AA' (β) stacking. (**a**−**b**) Simulated ADF images of two GaSe atomic layers with AB and AA' stacking, respectively. (**c**−**d**) Simulated profiles along the solid lines in (a) and (b), respectively. The profiles are in good agreement with the experimental results shown in insets of Figures 3d−f. (**e**−**f**) Schematic illustrations of bilayer GaSe with AB and AA' stacking, respectively.