Supporting Information

Wafer-Scale Growth of Single-Crystal 2D Semiconductor on Perovskite Oxides for High-Performance Transistors

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Materials and Methods

CVD growth of Bi$_2$O$_2$Se single-crystal films

Bi$_2$O$_2$Se single-crystal films were synthesized in a home-made CVD system equipped with a 110-cm horizontal tube furnace and 3-inch inner diameter quartz tube. Bi$_2$O$_3$ powder (Alfa Aesar, 99.999%) and Bi$_2$Se$_3$ powder (Alfa Aesar, 99.999%) were adopted as co-evaporation precursors to synthesize the Bi$_2$O$_2$Se films. Ar mixed with a small amount of oxygen (10 ppm) was used as the carrier gas to transport the vapor precursor to the growth region, where growth substrates of SrTiO$_3$ (001), LaAlO$_3$ (001), (La,Sr)(Al,Ta)O$_3$ (001) single crystals were located. The typical growth parameters for Bi$_2$O$_2$Se single-crystal films are as follows. The Bi$_2$O$_3$ powder was placed in the hot center and the Bi$_2$Se$_3$ powder was located upstream 5 cm with source temperature of about 660-675 °C. A total pressure of 300 Torr, growth temperature of 400 °C and growth time of 5-min were used. Remarkably, to demonstrate that the orientated nucleation of Bi$_2$O$_2$Se on the substrates, the growth temperature increased to 500 °C. The flow rate of Ar gas flow rate keeps around 200 s.c.c.m, which were regulated by a mass flow controller. To controllably synthesize the Bi$_2$O$_2$Se thin film, we monitored the growth time to fabricate films with the various thickness of quasi-monolayer (~5min), ~ 6 nm (15 min), ~10 nm (~20 min) and ~30 nm (~45 min).

Characterizations of Bi$_2$O$_2$Se thin films

The morphology of as-synthesized Bi$_2$O$_2$Se thin films was characterized using OM (Olympus DX51 microscope), AFM (Bruker icon), SEM (Hitachi S4800 field emission). The single crystallinity of Bi$_2$O$_2$Se thin film over a large scale was confirmed by a high-resolution X-ray diffraction system (Philips X-Pert Panalytical) with a Cu Ka1 radiation source (λ = 1.54056 Å). The electron backscatter diffraction measurements were performed on PHI 710 Auger Electron Spectrometer system which is equipped with an ultrahigh-sensitivity EBSD detector. Its spot size is 20 nm. The angular resolution of EBSD was ~0.1°, which allows for the confirmation of misorientation in subgrains or twin crystals. The cross sections of the epitaxial Bi$_2$O$_2$Se films on SrTiO$_3$ (001) substrates were imaged using Cs-corrected high-resolution STEM (Titan G2 80-200 ChemiSTEM, FEI). The cross-sectional samples for TEM testing were prepared using a focused ion beam (FIB) (Strata DB 235, FEI).
**Device fabrication and electrical transport measurements**

*Patterning Bi$_2$O$_2$Se films:* The Bi$_2$O$_2$Se thin film can be patterned to pre-designed regular arrays by our previously-reported region-selective chemical etching process with the assistance of photolithography. The etchant used has a component ratio of H$_3$O$^+$: H$_2$O$_2$: H$_2$O = 2:4:8. After steeping into the mixed etchant together with regular shaking for 10 s, the wafers were then quickly transferred to large quantities of water to terminate the etching reaction and avoid end-cutting effect. Finally, the wafers were further placed in acetone for 20 min to thoroughly remove the photoresist residue.

*Device Fabrications:* Both Hall-bar devices and the top-gate field-effect transistors were fabricated directly on as-etched Bi$_2$O$_2$Se patterns on the substrate. The standard photolithography overlay techniques were employed to construct multiple metal contacts and subsequent top-gate windows. Firstly, the positive photoresist of AR-P-5350 were spin-coated on the wafers, then followed by the UV illumination and exposed-area development by using the developer of the mixture of AR-P-300-26 and H$_2$O (volume ratio 1:7). Afterwards, the contact metal of Pd/Au (5 nm/40 nm) was deposition by thermal evaporation. Thirdly, the fabrication of top gate requires a second-step photolithography process, followed by atomic layer deposition (ALD) to grow the high-$\kappa$ top-gate dielectrics of HfO$_2$ (20 nm in thickness) and thermal evaporation to deposit the top-gate electrodes of Pd/Au (5 nm/40 nm).

*Electrical Measurements:* All the electrical measurements are performed at room temperature. Electrical measurement of top-gate FET behavior was carried out on a semiconductor analyzer (Keithley, SCS-4200) combined with a micromanipulator 6200 probe station under ambient condition. The transport measurements were performed in four-probe configurations in a Physical Properties Measurement Systems (PPMS, Quantum Design) with the superconducting magnets up to 9 T. The magnetic field applied is always perpendicular to the devices.
**Supplementary Text**

**Table S1.** The influence of interfacial interaction and lattice symmetry between three-fold \((C_3)\) symmetric 2D materials and substrate.

| Epilayer       | Substrate | Substrate Facet | Interaction             | Nucleation Orientation | Ref. |
|----------------|-----------|-----------------|-------------------------|------------------------|------|
| MoS\(_2\) \((C_3)\) | BN        | 001 \((C_3)\)   | van der Waals interaction | Disorder               | 1    |
| MoS\(_2\) \((C_3)\) | Mica      | 0001 \((C_3)\)  | van der Waals interaction | 0°, 60°                | 2    |
| MoS\(_2\) \((C_3)\) | Al\(_2\)O\(_3\) | 0001 \((C_3)\)  | van der Waals interaction | 0°, 60°                | 3    |
| MoS\(_2\) \((C_3)\) | Al\(_2\)O\(_3\) | 0001 \((C_3)\)  | van der Waals interaction | 0°, 60°                | 4    |
| MoS\(_2\) \((C_3)\) | Graphene  | 0001 \((C_6)\)  | van der Waals interaction | 12°                    | 5    |
| NbS\(_2\) \((C_3)\) | Graphene  | 0001 \((C_6)\)  | van der Waals interaction | 0°, 60°                | 6    |
| WS\(_2\) \((C_3)\) | BN        | 001 \((C_3)\)   | van der Waals interaction | 0°, 60°                | 7    |

As summarized in **Table S1**, the growth of conventional 2D TMD semiconductors of MX\(_2\) with three-fold symmetry usually adopt a van der Waals (vdWs) epitaxy mode on various substrates, regardless of their lattice mismatch. However, this vdWs epitaxy mode is detrimental to the achievement of wafer-scale 2D single crystals because of the presence of possible small-angle lattice rotations and the inevitable twinning behavior in multiple seeds, which may result in polycrystalline films with defective grain boundaries when they merge together, even on a symmetry and lattice constant matched single-crystal substrate.
Calculation of the lattice mismatch:

Small lattice mismatch between substrate and epilayer is beneficial to the epitaxial growth of high-quality films. Here, the lattice mismatch in our system is defined as:

$$\varepsilon_a = \left( \frac{a_{\text{Bi}_2\text{O}_2\text{Se}} - a_{\text{substrate}}}{a_{\text{substrate}}} \right) \times 100\%$$

Where $a_{\text{Bi}_2\text{O}_2\text{Se}}$ is lattice constant of Bi$_2$O$_2$Se. $a_{\text{substrate}}$ is lattice constant of STO, LAO, and LSAT substrates, respectively. To this end, the lattice mismatch ranges from +2.37% to -0.51% (see Table S2).

**Table S2.** Space groups, Lattice parameters, lattice distortions, and lattice mismatches of Bi$_2$O$_2$Se, SrTiO$_3$ (STO), LaAlO$_3$ (LAO), and (La, Sr)(Al, Ta)O$_3$ (LSAT)

| Materials       | Space Group | Lattice Parameters | In-plane Lattice Mismatches with Bi$_2$O$_2$Se |
|-----------------|-------------|--------------------|-----------------------------------------------|
| Bi$_2$O$_2$Se    | $I4/mmm$    | $a = b = 3.88 \text{ Å;}$ | 0 %                                           |
|                 |             | $c = 12.16 \text{ Å}$                                             |
| SrTiO$_3$       | $Pm-3m$     | $a = b = c = 3.90 \text{ Å}$                                      | -0.51 %                                      |
| (La,Sr)(Al,Ta)O$_3$ | $Pm-3m$ | $a = b = c = 3.87 \text{ Å}$                                      | -0.26 %                                      |
| LaAlO$_3$       | $Fm-3m$     | $a = b = c = 3.79 \text{ Å}$                                      | +2.37 %                                      |
Morphological characterization and phase confirmation of Bi₂O₂Se thin films

Large-area Bi₂O₂Se thin films were successfully grown on various wafer-size perovskite oxide substrates (1-inch STO, 1-inch LAO, and 2-inch LSAT) with different thicknesses (10 nm for Figure S1a, 30 nm for Figure S1b), which showed obviously different optical contrasts. Beside, with optimized condition, large-scale quasi-single-layer Bi₂O₂Se films (Figure S2-S4) were synthesized by applying a low supersaturation of precursor (i.e. lower growth temperature and higher system pressure). To this end, uniform Bi₂O₂Se thin films with tunable thickness from ~6 nm to ~10 nm were obtained by varying the growth time from 15 to 20 min (Figure S5), whose surface roughness is relatively small (0.3 nm) for the few-nm-thick one.

Figure S1. Photographs of large-area Bi₂O₂Se thin films grown on various wafer-size perovskite oxide substrates (1-inch STO, 1-inch LAO, and 2-inch LSAT) with growth time of ~20 min (a) and ~45 min (b), respectively.
Figure S2. Atomic force microscopy (AFM) characterizations of single-layer Bi$_2$O$_2$Se on SrTiO$_3$ (STO). AFM image (a) and the corresponding height profile (b) of as-synthesized monolayer Bi$_2$O$_2$Se film. Here, in order to conveniently characterize the monolayer Bi$_2$O$_2$Se, the growth time was decreased to 3 min to gain the monolayer Bi$_2$O$_2$Se island.

Figure S3. Atomic force microscopy (AFM) characterizations of quasi-single-layer Bi$_2$O$_2$Se film on STO as a function of growth time. (a) The bare STO substrate. (b-d) Morphological evolution of Bi$_2$O$_2$Se grown on STO with a growth time of 1 min, 3 min, and 5 min, respectively. (e) Large-area as-synthesized quasi-monolayer Bi$_2$O$_2$Se film with some second-layer islands on top of the underneath continuous single layer.

Figure S4. AFM characterization of single-layer Bi$_2$O$_2$Se film. (a) Photograph of monolayer Bi$_2$O$_2$Se film grown on STO. (b-f) The corresponding AFM images of monolayer Bi$_2$O$_2$Se sample collected at five discrete points.
Figure S5. AFM characterization of surface roughness of as-synthesized Bi$_2$O$_2$Se films. (a, b) Optical images of the Bi$_2$O$_2$Se films grown on STO substrates with a thickness of ~6 nm and ~10 nm (b), respectively. (c, d) AFM image and the corresponding height profile of as-synthesized Bi$_2$O$_2$Se film with a thickness of 6 nm (c), 10 nm (d) with a roughness ($R$) of 0.3 nm, and 0.6 nm respectively.

Figure S6. X-ray diffraction (XRD) analysis of Bi$_2$O$_2$Se films grown on LAO and LSAT substrates. (a, b) The $\theta$-2$\theta$ XRD patterns of films grown LAO (001) and LSAT (001) substrates. The single-crystalline Bi$_2$O$_2$Se phase shows that out-of-plane orientation is perfectly textured with the $c$ axis aligned perpendicular to the LAO (001) (a) and LSAT (001) (b) substrates plane. (c, d) Rocking curve for (004) reflection of Bi$_2$O$_2$Se film grown on the LAO (001) and LSAT (001) substrates, respectively.
**EBSD characterization of as-synthesized Bi$_2$O$_2$Se thin films**

**Figure S7.** Large EBSD maps of Bi$_2$O$_2$Se thin film. (a) SEM image taken over five consecutive 250×250 µm$^2$ areas across a Bi$_2$O$_2$Se film. (b-d) EBSD maps taken from the areas in (a), demonstrating the large-scale Bi$_2$O$_2$Se alignment. “Out-of-plane (z)” data shows the surface orientation, and the corresponding “In-plane (x)” and “In-plane (xy)” maps represent the azimuthal angle. Bottom: the inverse pole figure and orientation key for crystal orientation map.

**Figure S8.** EBSD characterization of a wafer-scale Bi$_2$O$_2$Se single-crystal film. (a) Photograph of Bi$_2$O$_2$Se films grown on 1-inch STO substrates. (b) EBSD pole figure of Bi$_2$O$_2$Se films. (c-k) EBSD maps taken from nine representative regions shown in (a).
**TEM characterization of as-synthesized Bi$_2$O$_2$Se thin films**

**Figure S9.** Crystalline mismatch characterization of epitaxial Bi$_2$O$_2$Se films on STO (001) substrate. (a) Cross-sectional HRTEM micrographs of the interface structures between STO and Bi$_2$O$_2$Se films. The right inset indicates a Fourier transform diffractogram corresponding to the Bi$_2$O$_2$Se/STO interface. The left inset shows a magnified view of the (200) diffraction pattern, suggesting long-range ordering of the interface structures. (b) Fourier-filtered images using FFT (200) diffraction spots corresponding to the HRTEM image in (a), demonstrating that there are no dislocations at the Bi$_2$O$_2$Se/STO interface.

**Figure S10.** Energy-dispersive X-ray Spectroscopy (EDX) image of the Bi$_2$O$_2$Se/STO (001) interface. (a) High angle annular dark-field (HAADF) image of a Bi$_2$O$_2$Se/STO interface and (b) corresponding elemental maps for Se, Bi, O, Sr, Ti, indicating that the Bi$_2$O$_2$Se/STO interface is abrupt.
**Electrical measurements of Bi$_2$O$_2$Se thin films**

**Figure S11.** Characterization of the spatial homogeneity of Bi$_2$O$_2$Se films. (a) Sheet resistance map of 1-inch wafer-size 2D Bi$_2$O$_2$Se film on STO. The wafer-scale spatial map of sheet resistance obtained from standard four-probe measurements of Bi$_2$O$_2$Se films with a thickness of ~20 nm, confirming that the as-grown Bi$_2$O$_2$Se film shows good uniformity of the electrical properties on a wafer scale. The sheet resistance was measured using a four-probe system (CDE ResMap 178) based on the four-point probe method to eliminate contact resistance. Four metal probes were aligned in a line at an interval of 1 mm. (b) Four-probe resistance measurements of the Bi$_2$O$_2$Se film with different channel lengths. Linear curve of 4-probe resistance versus channel length from 2 μm to 1000 μm reveals the uniform distribution of conductivity of Bi$_2$O$_2$Se thin films. Left-top inset shows the SEM image of Bi$_2$O$_2$Se device in the four-terminal configuration (identical channel width). All the measurements were performed at a voltage ($V_{DS}$) of 1 V between source and drain electrodes.
Figure S12. Hall mobility evaluation of Bi$_2$O$_2$Se thin films grown on STO substrate. (a) Optical microscopy image of as-grown Bi$_2$O$_2$Se films (~10 nm in thickness) device with an etched Hall bar configuration. (b) Room-temperature Hall measurement of the 2D Bi$_2$O$_2$Se film with a thickness of ~10 nm. The negative slope of $R_{xy}$-$B$ indicates the n-type behavior of as-synthesized 2D Bi$_2$O$_2$Se. Hall mobility of this device with is about 94 cm$^2$ V$^{-1}$ s$^{-1}$ at 300 K, which is similar to the field-effect mobility. (c) Resistance ($R_{xx}$) as a function of temperature of the discrete Bi$_2$O$_2$Se nanoplate with a thickness of ~20 nm. Inset: optical microscopy image of a Hall-bar device fabricated on the Bi$_2$O$_2$Se nanoplate. Hall mobility of this particular device is ~120 cm$^2$ V$^{-1}$ s$^{-1}$ at 300 K, slightly larger than the value of etched sample. (d) $\mu_{Hall}$ of Bi$_2$O$_2$Se Hall-bar device as a function of channel length. All the devices showed similar Hall mobility of ~100 cm$^2$ V$^{-1}$ s$^{-1}$, independent of channel length, and device location.

Figure S13. Gate-dependent source-drain current ($I_{DS}$) of three typically additional 10-nm-thick Bi$_2$O$_2$Se FETs devices with different channel lengths.
Figure S14. (a) OM image of the top-gated FET based on 5-nm-thick Bi$_2$O$_2$Se thin films grown on STO. (b) The corresponding AFM image and height profile of Bi$_2$O$_2$Se FET (red marked in a). (c) Transfer curve of 5-nm Bi$_2$O$_2$Se FET, showing high on/off ratio of $>$10$^7$ and high field-effect mobility of $\sim$85 cm$^2$ V$^{-1}$ s$^{-1}$.

Figure S15. Statistics for electrical performance of Bi$_2$O$_2$Se FETs array. (a) Optical image of a 6×6 Bi$_2$O$_2$Se FETs array fabricated on the SrTiO$_3$ substrate. (b, c) Histograms of drive current (b) and mobility (c) of a 6×6 Bi$_2$O$_2$Se FETs array, showing a high drive current of $\sim$20 μA μm$^{-1}$, a high mobility of $\sim$150 cm$^2$ V$^{-1}$ s$^{-1}$.
Table S3. Comparison of electrical performance at room temperature for CVD-grown and solution-processed 2D semiconductor thin films.

| Materials | Synthesis Approach | Mobility (cm²V⁻¹s⁻¹) | Ref. |
|-----------|--------------------|------------------------|------|
| MoS₂      | Solution-processed thin-film | 7–11                   | 8    |
|           |                     | ~0.5                   | 9    |
|           |                     | ~0.4                   | 10   |
|           | CVD-grown thin-film | 30                     | 11   |
| MoSe₂     | Solution-processed thin-film | 0.18                   | 9    |
|           | CVD-grown thin-film | 23                     | 13   |
| Bi₂O₂Se   | CVD-grown thin-film | 150                    | This work |

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