Supporting Information for

Van der Waals epitaxial growth of atomically thin Bi$_2$Se$_3$ and thickness-dependent topological phase transition

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1. AFM images and morphologies of as-grown ultrathin Bi$_2$Se$_3$

Figure S1 shows typical morphologies of as-grown ultrathin Bi$_2$Se$_3$ on h-BN substrates. The sample thickness was determined by AFM.

Figure S1: AFM images of as-grown ultrathin Bi$_2$Se$_3$ with different thicknesses on h-BN: a, 2 QLs, b, 3QLs, c, 4 QLs, d, 5 QLs, e, 6 QLs, f, 8 QLs. The thickness of one quintuple layer is about 1 nm. The height profiles along the dotted lines are attached at the bottom of corresponding images.
2. AFM images for h-BN/Bi$_2$Se$_3$/h-BN sandwiched heterostructures.

Figure S2 demonstrates the AFM images of the h-BN/Bi$_2$Se$_3$/h-BN sandwiched heterostructures fabricated by our dry transfer process. The sample demonstrated here has 2 QLs and the top h-BN transferred is about 4.7 nm thick. A small part of Bi$_2$Se$_3$ was deliberately exposed by the top h-BN during the transfer process. The accuracy of the transfer process achieved in this work is less than 2 µm.

![AFM images](image)

**Figure S2**: AFM images demonstrate the sample **a**, before and **b**, after the mechanical transfer process. The height profiles along the dotted lines are attached at the bottom of corresponding images.
3. The growth behavior of Bi$_2$Se$_3$ on h-BN surfaces.

Bi$_2$Se$_3$ can grow across the steps (Figure S3) or edges (Figure S4) on h-BN surfaces. The steps have been identified by the contrast in the optical images in Figure S3a and S3b. Different contrasts represent different thicknesses of h-BN. The thickness of Bi$_2$Se$_3$ was uniform (almost no change after crossing over the h-BN steps) according to the AFM data shown in Figure S3c.

Figure S3: a, b, are optical images of Bi$_2$Se$_3$ thin-layers grown on h-BN step edges. c, is the AFM image of the sample shown in b.

Figure S4: A Bi$_2$Se$_3$ single crystal shows a regular shape across h-BN edges.
4. The growth behavior of $\text{Bi}_2\text{Se}_3$ on $\text{SiO}_2/\text{Si}$ substrates

For long-duration growth, $\text{Bi}_2\text{Se}_3$ also formed directly on the surfaces of $\text{SiO}_2/\text{Si}$ substrates. However, the growth rate was much lower than that on h-BN. Figure S5 shows the optical image of the $\text{Bi}_2\text{Se}_3$ crystals formed on a $\text{SiO}_2/\text{Si}$ substrate for two minute growth. The thicknesses marked in the figure were determined by AFM. The size of these $\text{Bi}_2\text{Se}_3$ nano-plates grown on $\text{SiO}_2/\text{Si}$ substrates was small and their orientations were random. By increasing growth duration, $\text{Bi}_2\text{Se}_3$ became thicker and finally formed a continuous thin film. However, these samples are not suitable for capacitance measurement.

Figure S5: An optical image showing $\text{Bi}_2\text{Se}_3$ crystals directly grown on the $\text{SiO}_2/\text{Si}$ substrate.
5. Double diffractions from Bi$_2$Se$_3$ and h-BN

By comparing the selected-area electron diffraction (SAED) patterns with simulation results (see Figure S6), we identified that the inner diffraction spots in Figure 3b and five additional spots in Figure 3c were from double diffractions. In Figure S6, the black circles (or dots) are diffraction spots from h-BN. The red ones are diffraction spots from Bi$_2$Se$_3$. The blue ones are due to the double diffraction of Bi$_2$Se$_3$ generated by \{1\bar{1}00\} planes of h-BN. The pinks ones are due to the double diffraction of Bi$_2$Se$_3$ generated by \{11\bar{2}0\} planes of h-BN. The yellow ones are due to the double diffraction of Bi$_2$Se$_3$ generated by \{2\bar{2}00\} planes of h-BN. The spots size and color intensity in c, d represent the relative diffraction intensity. The strong transmitted beams at the center positions in a, b were blocked in order to protect the CCD camera in TEM.
Figure S6: Comparison between experimental SAED patterns and simulation results. a, b, are experimental results. c, d, are simulation ones. a, c, are the case for ‘P2’ in Figure 3a. b, d, are the case for ‘P3’.

6. Moiré patterns from h-BN overlapped with Bi₂Se₃

The periods of the Moiré patterns observed in our samples were analyzed. Since the diffractions from the \{11\overline{2}\} planes of Bi₂Se₃ are forbidden, the Moiré pattern generated from the Bi₂Se₃/h-BN superlattice is based on h-BN \{11\overline{2}\} and Bi₂Se₃ \{11\overline{2}0\} planes. Therefore, the corresponding lattice spacing vectors are \( a = a_{BN} = 0.2504 \) nm for h-BN and \( b = a_{Bi₂Se₃}/\sqrt{3} = 0.2393 \) nm for Bi₂Se₃. Then the reciprocal lattice vectors can be described as \( |\vec{k}_{BN}| = \frac{2\pi}{a} \) for h-BN and \( |\vec{k}_{Bi₂Se₃}| = \frac{2\pi}{b} \) for Bi₂Se₃. The Moiré vector is then obtained as: \( \vec{k}_{Moiré} = \vec{k}_{BN} - \vec{k}_{Bi₂Se₃} \). The period of the moiré pattern is given by

\[
\lambda = \frac{2\pi}{|\vec{k}_{Moiré}|} = \frac{2\pi}{|\vec{k}_{BN} - \vec{k}_{Bi₂Se₃}|} = \frac{(1+\delta)a}{\sqrt{2(1+\delta)(1-\cos\theta)+\delta^2}}
\]

where \( \delta = \frac{b-a}{a} \) is the mismatch between h-BN and Bi₂Se₃, \( \theta \) is the angle between \( \vec{k}_{BN} \) and \( \vec{k}_{Bi₂Se₃} \).

7. Lorentz fitting of the Raman data

The peak position and intensity in the Raman data were determined according to the Lorentz fitting. The typical fitting results are shown in Figure S7.
Figure S7: Lorentz fitting of the typical Raman data shown in the main text. a-e, show the data obtained from the samples on SiO$_2$/Si substrates, f-j, show the data obtained from the samples on h-BN.

8. Raman enhancement effects in Bi$_2$Se$_3$/h-BN structures

For the Bi$_2$Se$_3$ samples formed on h-BN, the Raman intensities are significantly influenced by the thickness of h-BN. Figure S8 shows the Raman spectra of 2 QLs Bi$_2$Se$_3$ on the h-BN flakes with different thicknesses. The thicknesses of Bi$_2$Se$_3$ and h-BN were determined by AFM. As mentioned in the main text, the different optical contrasts we observed indicated different thicknesses of h-BN substrates. The positions of the Raman peaks (e.g., $A_{1g}^2$) are not sensitive to the thickness of h-BN. However, the Raman intensity varies significantly for different thicknesses of h-BN. As evidenced in Figure S9, the 6 QLs Bi$_2$Se$_3$ grew across h-BN edges (e.g. at positions ‘A’ and ‘B’ have) resulting in significantly change of the Raman intensities.
Figure S8: Raman spectra of 2 QLs Bi₂Se₃ formed on h-BN substrates with different thicknesses. The scale bars in a-f are 5 µm.
Figure S9: Raman spectra of a 6 QLs Bi$_2$Se$_3$ grown across a h-BN edge. a, shows different optical colors at positions ‘A’ and ‘B’ which are originated from different thicknesses of h-BN. b, c, are the Raman mapping by choosing $E_g^2$ and $A_{1g}^2$ peaks, respectively. d, is the Raman spectra obtained at the positions ‘A’ and ‘B’ marked in a.

9. Modeling of the interference, optical contrast and Raman enhancement effects in Bi$_2$Se$_3$/h-BN

The optical interference$^2$ occurring in the Bi$_2$Se$_3$/h-BN structures resulted in the changes of optical contrast and Raman intensity in our samples. Based on the framework of classical optics, our samples consist of five media: air, Bi$_2$Se$_3$, h-BN, SiO$_2$ and Si.
Multiple reflections and refractions occur at all interfaces as shown in Figure S10a. The complex index of each dielectric is $n_i = n_i - ik_i$, where $i = 0, 1, 2, 3, 4$ represent air, Bi$_2$Se$_3$, h-BN, SiO$_2$ and Si, respectively. Then, the Fresnel reflection and transmission coefficients are $r_{ij} = \frac{n_i - n_j}{n_i + n_j}$, $t_{ij} = \frac{2n_i}{n_i + n_j}$. Considering the h-BN/SiO$_2$ interface, the effective reflection coefficient can be calculated by:

$$ r' = r_{23} + t_{23} e^{-i\beta_3} r_{34} e^{-i\beta_3} t_{32} + ... = \frac{r_{23} + r_{34} e^{-2i\beta_3}}{1 + r_{23} r_{34} e^{-2i\beta_3}} $$

where $\beta_i = 2\pi n_i \frac{d_i}{\lambda}$ is the phase increment when the incident light travels across the media. The effective reflection coefficients are $r'' = \frac{r_{12} + r' e^{-2i\beta_2}}{1 + r_{12} r' e^{-2i\beta_2}}$ for Bi$_2$Se$_3$/h-BN interface and $r''' = \frac{r_{01} + r'' e^{-2i\beta_1}}{1 + r_{01} r'' e^{-2i\beta_1}}$ for air/Bi$_2$Se$_3$ interface.

The optical contrast can be defined as the relative intensity of reflected light in the presence and absence of Bi$_2$Se$_3$:

$$ C(\lambda) = \frac{I_{BN}(\lambda)/BI_{2Se3}(\lambda)}{I_{BN}(\lambda)} $$

where, $I_{Bi2Se3}(\lambda) = (r''')^* r'''$. $I_{BN}(\lambda)$ represents the intensity of reflected light in the air/h-BN/SiO$_2$/Si system, which can be calculated by $I_{BN}(\lambda) = (r''')^* r'''(n_1 = n_0 = 0)$.

In the Raman measurements, the net absorption can be calculated by the summation of the absorptions in Figure S10c, which gives

$$ F_{ab} = t_{01} \frac{e^{-i\beta_x} + r'' e^{-i(2\beta_1 - \beta_x)}}{1 + r'' r_{01} e^{-2i\beta_1}}. $$

The emission term from depth $x$ by the summation in Figure S10d can be expressed as
\[ F_{sc} = t_0 \frac{e^{-i(\beta_x + \gamma')}}{1 + r'' r_0 e^{-2i\beta_1}}. \]

Then the total enhancement factor is given by \( F = N \int_0^{d_1} |F_{ab} F_{sc}|^2 \, dx \), where \( N \) is a normalization factor. The measured Raman intensity is \( I = I_i F \), where \( I_i \) is the intrinsic Raman intensity.

Figure S10: a, Schematic diagram of multiple reflection and refraction at the five media system. b, Schematic diagram for calculating the effective reflection at the h-BN/SiO₂ interface. This method can be applied to the Bi₂Se₃/h-BN and air/Bi₂Se₃ interfaces. Interference enhanced Raman processes are schematically shown in c, the absorption process and d, the emission process. The dots represent the points of interaction between the laser beam and Bi₂Se₃.
10. Device structure of h-BN/Bi₂Se₃/h-BN for transport characterization

The top h-BN layer is very critical and specially chosen to fit the Bi₂Se₃ sample. During the transfer process, both source and drain regions were exposed for metal electrode deposition (see Figure S11).

Figure S11: Device structure for transport measurement. a, The as-grown Bi₂Se₃ on h-BN. b, AFM image of the sample shown in a. c, after transferring the top h-BN layer. d, The final device connected with metal electrodes.

11. Capacitance data for 2 QLs and 5 QLs samples

The measured capacitance of 2 QLs sample is shown in Figure S12. At 2K, the Fermi level can be tuned into the bandgap at about -2.5 V. The valence band edge was not
observed in this sample. The charges trapped in the conduction band edge were gradually excited as temperature increases.

Figure S13 shows the capacitance of 5 QLs sample measured at different temperatures. Obviously, no mid-gap states were observed even in the high temperature range, indicating the high quality of this sample. When sample temperature was increased, the band edges became broadened and the insulating behavior in the gap was suppressed, resulting in a narrowed flat region in Figure S13. We observed Landau quantization behavior under high magnetic fields as shown in Figure S14.

Figure S12: The capacitance data measured at different temperatures for 2 QLs samples.
Figure S13: The capacitance data measured at different temperatures for 5 QLs samples.

Figure S14: Landau quantization in the 5QLs sample. The Landau level induced peaks in the surface states are marked by the arrows.
12. Depletion and quantum capacitance

For thick Bi$_2$Se$_3$ samples, the gate voltage induced band bending over the depletion region will contribute to the total capacitance, which is known as the depletion capacitance. In this case, the profiles of the charge density $\rho(x)$ and the electrostatic potential $\varphi(x)$ distribution are changed as shown in Figure S16. Setting the origin $x = 0$ at the surface of Bi$_2$Se$_3$, the charge density can be expressed by

$$\rho(x) = -\frac{e}{A} \delta(x + s) + \sigma_s \delta(x) + N_d ed [\theta(x) - \theta(x - d)],$$

where $\sigma_s$ is the surface charge density, $N_d$ the density of ionized donor impurities at the depletion region, $d$ the width of the depletion layer, $A$ the area and $\theta(x) = \begin{cases} 0, & x \leq 0 \\ 1, & x > 0 \end{cases}$ the step function. Then the Poisson equation is

$$-\frac{\partial^2 \varphi(x)}{\partial x^2} = \frac{\rho(x)}{\varepsilon_0 \varepsilon(x)},$$

where $\varepsilon_0$ is the vacuum permittivity and $\varepsilon(x)$ the dielectric constant. $\varepsilon(x) = \varepsilon_{Bi_2Se_3}$ when $x > 0$, and $\varepsilon(x) = \varepsilon_{BN}$ when $-s < x < 0$. By solving the Poisson equation, we can get the electric field and potential distribution. If we set $\varphi$ and $\partial \varphi / \partial x$ to 0 in the bulk region, the potential distribution in Bi$_2$Se$_3$ is

$$\varphi(x) = -\frac{N_d e}{2\varepsilon_0 \varepsilon_{Bi_2Se_3}} (x - d)^2 \quad (x > 0).$$

Specifically, the electric field near $x = 0$ is $E(0^+) = -N_d ed / \varepsilon_0 \varepsilon_{Bi_2Se_3}$, $E(0^-) = -(\sigma_s + N_d ed) / \varepsilon_0$. This means that the electric field is partially screened by surface charges and penetrates into the depletion layer and further screened by the ionized donor charges.
Because of charge conservation, we have:

\[ \frac{Q}{A} = N_d e d + \sigma_s. \]

The charge in the first term of the right \((N_d ed)\) induced by \(\varphi(0) = -\frac{N_d e d^2}{2 \varepsilon_0 \varepsilon_{Biz}\varepsilon_3}\) in the depletion region defines the depletion capacitance \(C_d = \frac{N_d ed A}{\varphi(0)} = \\varepsilon_0 \varepsilon_{Biz}\varepsilon_3 A/d\). The surface charges in the second term \((\sigma_s)\) induced by \(\varphi(0)\) is the quantum capacitance \(C_q = \frac{\sigma_s}{\varphi(0)} = e^2 (d\nu_s/d\mu)\). Clearly, \(C_d\) and \(C_q\) are in parallel connection, which can be measured experimentally (see the data shown in Figure 5d for 16 QLs sample).
Figure S15: Schematic for the band bending and the distributions of charges, electric field and potential in our capacitance devices.
13: Shubnikov-de Hass (SdH) oscillations for Dirac fermion in the surface states

The existence of Dirac fermion in the surface states of Bi$_2$Se$_3$ topological insulators (TIs) (≥6 QLs) can be proven not only by the linear $E - k$ relation (Figure 4c), but also by the SdH oscillations. Figure S5 shows the magnetoresistance (MR) of 12 QLs Bi$_2$Se$_3$ samples. Despite of the large background in the MR curve (as shown in Figure S16a) originating from the bulk conduction, SdH oscillations is visible by performing second derivative $-\frac{d^2R}{dB^2}$ to the curve$^5$ as plotted in Figure S16b. The oscillation amplitude against the inverse of magnetic fields ($B$) can be described by $-\frac{d^2R}{dB^2} \sim \cos[2\pi(\frac{F}{B} + \frac{1}{2} + \gamma)]$, where $F$ is the oscillation frequency and $2\pi\gamma$ denotes the phase factor. The unusual Berry’s phase in Dirac fermions requires $\gamma = 0.5$. The oscillation frequency can be obtained by performing the fast Fourier transform (FFT). Figure S16c gives $F = 61$ T. The frequency is directly related to the size of Fermi surface described by Onsager equation: $F = (\frac{\hbar}{2\pi e})A$, where $A = \pi k_F^2$ is the Fermi surface area. The carrier density in the 2D surface of TIs is determined by $n = \pi k_F^2 / (2\pi)^2$. The carrier density contributed by the surface states is calculated to be about $1.47 \times 10^{12}$ cm$^{-2}$. By fitting the Landau level index as a function of $1/B$ with $N = \left(\frac{e}{B}\right) + \alpha$ (Figure S17d), we get the intercept of 0.48, very close to 0.5. This indicates that the SdH oscillations originate from the surface Dirac fermion.
Figure S16: SdH oscillations in the 12 QLs Bi$_2$Se$_3$ sample. **a**, The MR data. **b**, The oscillation plotted in $-\frac{d^2R}{dB^2}$ versus $1/B$. **c**, The FFT result based on the data shown in **b**. **d**, The Landau level fan diagram plot employing a valley in **b** as an integer $N$. Red line is the linear fit.

**Reference**


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