

Preservation of Topological Surface States in Millimeter-Scale Transferred Membranes

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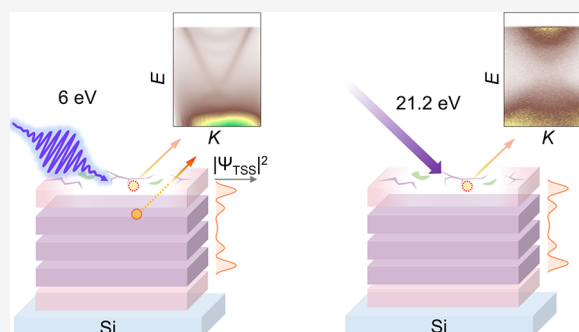
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ABSTRACT: Ultrathin topological insulator membranes are building blocks of exotic quantum matter. However, traditional epitaxy of these materials does not facilitate stacking in arbitrary orders, while mechanical exfoliation from bulk crystals is also challenging due to the non-negligible interlayer coupling therein. Here we liberate millimeter-scale films of the topological insulator Bi_2Se_3 , grown by molecular beam epitaxy, down to 3 quintuple layers. We characterize the preservation of the topological surface states and quantum well states in transferred Bi_2Se_3 films using angle-resolved photoemission spectroscopy. Leveraging the photon-energy-dependent surface sensitivity, the photoemission spectra taken with 6 and 21.2 eV photons reveal a transfer-induced migration of the topological surface states from the top to the inner layers. By establishing clear electronic structures of the transferred films and unveiling the wave function relocation of the topological surface states, our work lays the physics foundation crucial for the future fabrication of artificially stacked topological materials with single-layer precision.

KEYWORDS: *topological insulator, Bi_2Se_3 film, millimeter-scale transfer, ARPES*



Van der Waals (vdW) materials, exemplified by graphene and transition metal dichalcogenides, provide versatile material platforms to realize fascinating topological^{1–5} and strongly correlated phases of matter.^{6–10} The vdW interactions between the 2D layers enable convenient mechanical exfoliation and reassembly of new heterostructures. However, it is notably challenging to employ traditional exfoliation to produce ultrathin topological insulator (TI) films, such as Bi_2Se_3 ^{11–13} and Bi_2Te_3 ,^{14,15} with uniform thicknesses. This is due to the stronger orbital overlap between the outer chalcogen atoms in the TI films. In a recently developed approach termed “remote epitaxy”, thin films are fabricated on top of graphene-coated substrates followed by releasing of the epitaxial layers via mechanical exfoliation.¹⁶ However, this method requires delicate control of the graphene buffer layer and the graphene–substrate interface and has not been implemented on a wide variety of materials such as the TIs. Another exfoliation protocol employs gold coating on silicon to exfoliate and transfer Bi_2Se_3 , but this approach does not enable accurate control of the film thickness over a large spatial scale.¹⁷ If one can transfer TI membranes with precisely controlled thicknesses at spatial scales larger than 1 mm, many revenue opportunities such as the construction of superlattices, devices, twistrionics, and suspended films will be opened up,

enabling new approaches to electronics, spintronics, and quantum informatics.

By etching the oxide layer at the oxide–chalcogenide interface, Bansal et al. separated molecular beam epitaxy (MBE)-grown Bi_2Se_3 thin films from oxide substrates.¹⁸ This pioneering study highlighted the possibility of assembling new heterostructures using MBE-grown, wafer-scale films, yet it remains to be seen whether the electronic structure is preserved after the harsh chemical processing. In particular, it is unclear whether the key electronic state for TI films, the topological surface state (TSS), survives the chemical treatment. In this work, we employ angle-resolved photoemission spectroscopy (ARPES) to characterize a series of Bi_2Se_3 ultrathin films with thicknesses ranging from 3 to 10 quintuple layers (QLs) and reveal the electronic structure changes after a millimeter-scale liberation. Our ARPES data using 6 eV photons suggest that despite contamination-induced spectral

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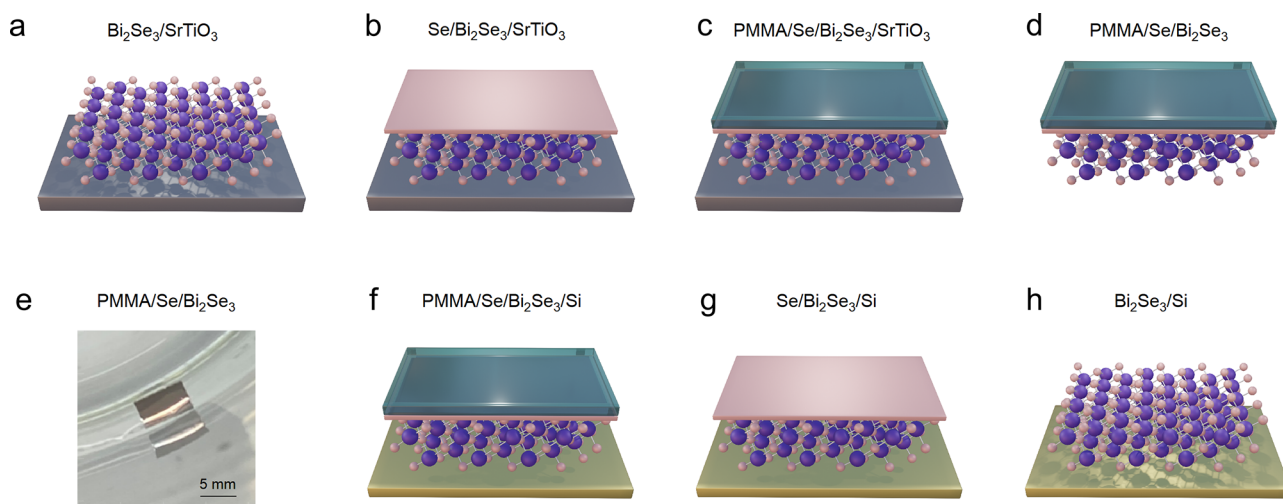


Figure 1. Schematics of the liberation process. (a) A Bi_2Se_3 thin film was grown on an oxide substrate SrTiO_3 by MBE. (b) An amorphous selenium capping layer was deposited on the sample. (c) A layer of poly(methyl methacrylate) (PMMA) was spin-coated on top of the sample. (d) The Bi_2Se_3 thin film supported by PMMA was liberated from SrTiO_3 using buffered oxide etchant. (e) Photograph of a liberated 6 QL Bi_2Se_3 film with the lateral dimensions of $10 \times 5 \text{ mm}^2$. (f) The liberated film was transferred to a target substrate (Si). (g) The PMMA layer was dissolved in acetone. (h) The Se capping layer was removed by annealing in the MBE chamber.

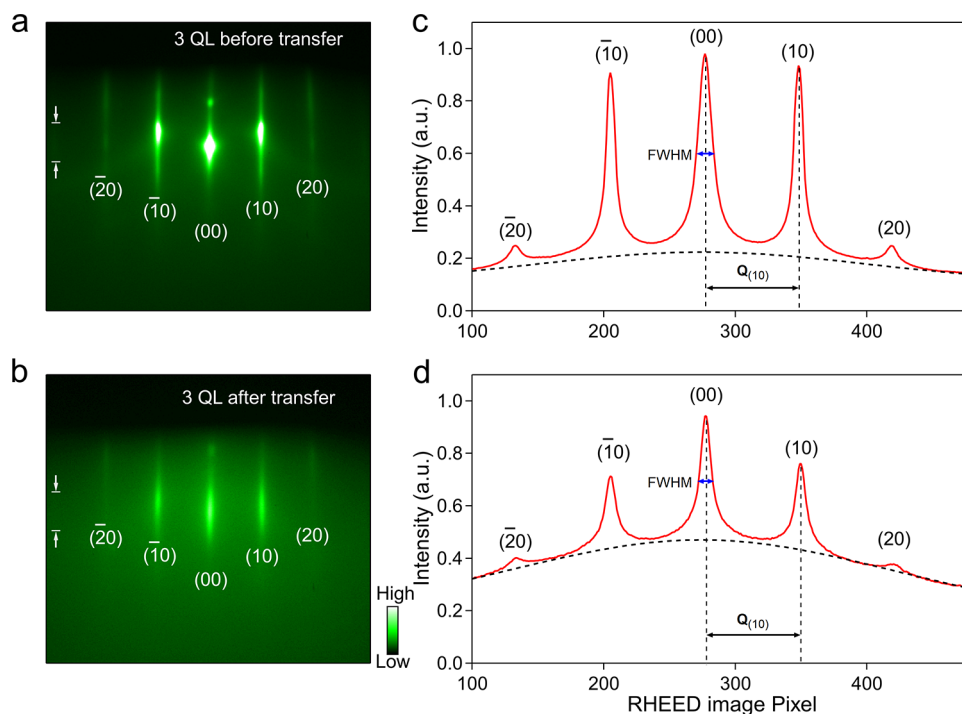


Figure 2. Reflection high-energy electron diffraction (RHEED) patterns of Bi_2Se_3 films taken with the electron beam along the $[11\bar{2}0]$ direction. (a) RHEED image of an as-grown 3 QL Bi_2Se_3 film on SrTiO_3 substrate. (b) RHEED image of a transferred 3 QL Bi_2Se_3 film on Si. (c, d) The line profiles (red lines) of the RHEED images in (a) and (b), respectively. The integration ranges of the line profiles are marked by white arrows in (a) and (b). The black dashed thick lines are the backgrounds extracted by fitting the profiles using Gaussian functions. The signal-to-background ratios at the (00) peaks in (c) and (d) are around 3 and 1, respectively. The full-widths at half-maximum (fwhm) of the (00) peaks and the distances between the (00) and (10) peaks are marked by blue and black arrows, respectively.

broadening, the key electronic structures including the TSS and the quantum well states (QWSs) are largely preserved after transferring the entire Bi_2Se_3 film from an SrTiO_3 substrate to a Si substrate. This result establishes the material physics foundation for further manipulation of such TI films for twistrionics and topotronics. Interestingly, our ARPES spectra taken with 21.2 eV photons on the same set of samples display no signatures of the TSS and diffusive features of other

electronic bands. Considering the extreme surface sensitivity of 21.2 eV photoemission,¹⁹ our work reveals the wave function relocation of the TSS from the top layer to the inner layers. This discovery has direct implications on the topology of the liberated TI films and the functionalities of future devices utilizing them.

Figure 1 illustrates the step-by-step protocol of liberating and transferring Bi_2Se_3 films with a lateral dimension of 10×5

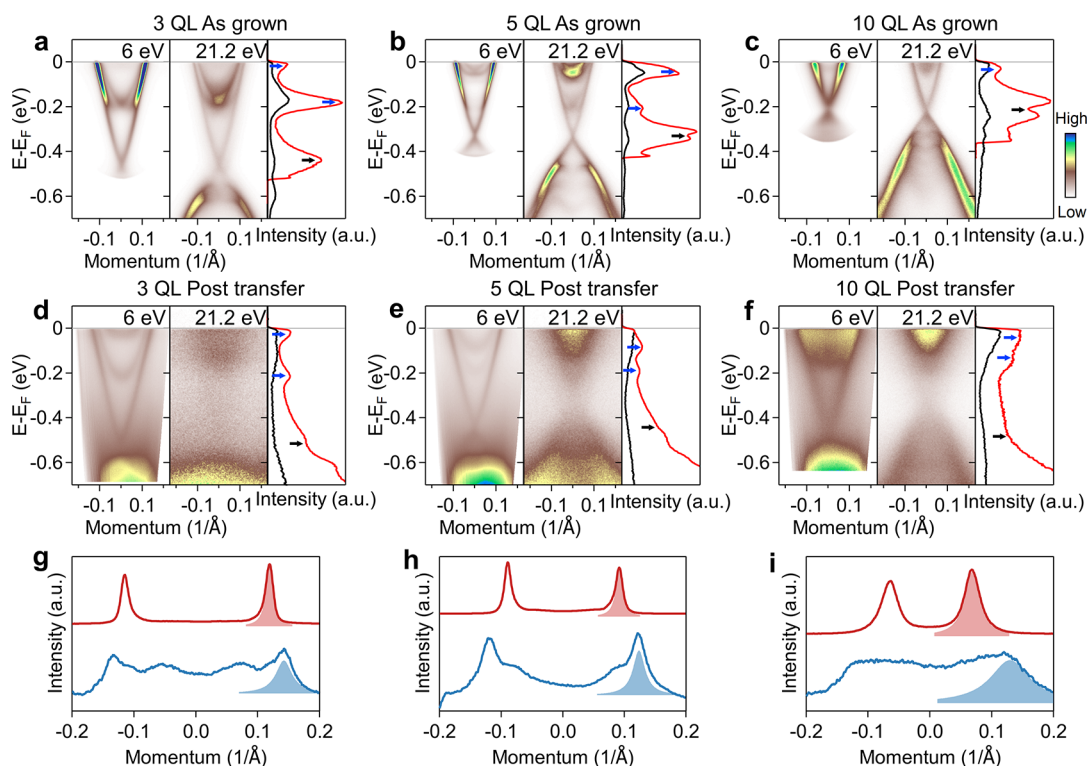


Figure 3. ARPES spectra of the as-grown and transferred Bi_2Se_3 films along the Γ –K direction. (a–c) Band structures near Γ of as-grown (a) 3 QL, (b) 5 QL, and (c) 10 QL Bi_2Se_3 films. (d–f) Band structures near Γ of exfoliated (d) 3 QL, (e) 5 QL, and (f) 10 QL Bi_2Se_3 films. ARPES spectra taken with 6 and 21.2 eV photons are compared in each of the (a–f). Red and black lines in (a–f) are the energy distribution curves (EDCs) taken at Γ using photon energies of 6 and 21.2 eV, respectively. Black and blue arrows mark the positions of the Dirac point and the quantum well states, respectively. (g–i) Momentum distribution curves (MDCs) taken at the Fermi level of the as-grown (red) and transferred (blue) Bi_2Se_3 films, using 6 eV photons. Red and blue shaded areas illustrate the Lorentzian functions used to fit the peaks corresponding to the topological surface states.

mm^2 . Bi_2Se_3 is first grown on an oxide substrate, SrTiO_3 (111), using MBE (Figure 1a). The growth recipe is described in detail in Methods. Selenium capping after growth (Figure 1b) is crucial for protecting the film's surface morphology against contamination from the polymer and the etchant used in later steps. Subsequently, the film is taken out of ultrahigh vacuum and a layer of poly(methyl methacrylate) (PMMA) is spin-coated on top of the selenium-capped film (Figure 1c). The PMMA layer is cured after baking at 80 °C for 10 min. The sample is then floated on buffered oxide etchant (BOE; $\text{HF}:\text{NH}_4\text{F} = 7:1$), where the film peels itself off due to etching reactions at the film–substrate interface (Figure 1d,e). The floated film can be fished out using any desired substrate or device (Figure 1f). To facilitate ARPES measurements, the PMMA and Se layers are removed using acetone and 200 °C vacuum annealing, respectively (Figure 1g,h).

We perform reflection high energy electron diffraction (RHEED) characterization of the films to compare the surface morphology before and after the transfer. During the growth, the RHEED intensity at the specular peak undergoes strong oscillations (Supporting Information (SI) Note 1), allowing us to precisely determine the thickness. The RHEED image taken from an as-grown 3 QL Bi_2Se_3 film shows streaks with a typical full-width at half-maximum (fwhm) of 13 pixels, which corresponds to 18% of the distance between the zeroth- and first-order streaks in the reciprocal space (Figure 2c). The signal-to-background ratio is near 3, as measured by the intensity ratio of the [00] streak and its baseline at the peak position. These observations indicate the two-dimensionality

and high crystallinity of the film. After the millimeter-scale transfer process, the RHEED pattern of the post-transfer film (Figure 2b) is highly consistent with the as-grown film (Figure 2a). The average fwhm of 12 pixels is comparable to the result from the as-grown film, while the signal-to-background ratio is reduced to 1 (Figure 2d). This is possibly due to the residue resulting from the polymer and other chemicals involved in the transfer process. Despite selenium capping, a small amount of surface oxidation may also contribute to the background in the RHEED image. Nevertheless, the sharp streaks remain visible, suggesting that the surface morphology and crystallinity of the film are largely preserved after transfer. This is corroborated by atomic force microscopy (AFM) and Raman spectroscopy measurements on the transferred Bi_2Se_3 films (SI Note 2).

We utilized ARPES to directly measure the electronic structures of the Bi_2Se_3 films before and after the transfer. Figure 3a–c shows the band structures of the as-grown Bi_2Se_3 films with different thicknesses at 8.5 K. Results taken with 6 and 21.2 eV photons are compared. Notably, low-energy cutoffs (LECs) are observed at -0.52 , -0.42 , and -0.36 eV for 3 QL, 5 QL, and 10 QL films, respectively, in the 6 eV ARPES spectra. The kinetic energy corresponding to the LEC is precisely the work function difference between the sample and the photoemission detector (SI Note 3).²⁰ Using 21.2 eV photoemission, the kinetic energies for the electrons near the Fermi level (E_F) are in the range of 16–17 eV, not affected by the LEC. The TSSs with quasi-linear band dispersions are clearly observed. Compared to a previous study on ultrathin Bi_2Se_3 films,²¹ our ARPES data using the same photon energy

of 21.2 eV feature sharper TSS band dispersions (Figure 3a–c, Figure S4). Notably, when the thickness is ≤ 3 QL the TSSs from the top and bottom surfaces are expected to hybridize.²¹ To avoid the complication due to the LEC, we use 21.2 eV photons and resolve a subtle hybridization gap of ~ 60 meV near $E - E_F \approx -0.52$ eV in the 3 QL film (Figure S3d), and a substantial gap of ~ 200 meV in the 2 QL film (Figure S4b). For thicknesses ≥ 5 QL, 40–60 meV gaps are seemingly observed at the Dirac point (Figure 3b,c, Figure S5), whereas this Dirac gap is expected to be < 4 meV by first-principles calculations.²² With a careful analysis of the thickness and photon-energy dependence of the Dirac gaps (SI Note 4), we conclude that the apparent Dirac gaps in 5 QL and 10 QL films before the transfer are likely due to a line width broadening effect, where the energy and momentum smearing leads to an apparent double-peak structure in the energy distribution curve at zero momentum (Figure 3b,c),²³ not reflecting the intrinsic physics in the materials. The Dirac point is systematically shifted to deeper binding energies as the film becomes thinner (Figure 3a–c), which is also consistent with previous observations.²¹ This is likely due to the band bending arising from the charge transfer between the substrate and the Bi_2Se_3 film.

In addition, QWSs induced by the quantum confinement are particularly clear in the 3 QL and 5 QL films (Figure 3a,b).²¹ We performed a systematic thickness-dependent study of the QWSs (SI Note 5). Theoretically, the energy difference between the n th- and zeroth-order QWSs (ΔE_{n-0}) for an infinite-depth quantum well scales with n^2/d^2 , where d is the film thickness.²² In our experiment, we extract the exponent of the ΔE_{1-0} versus d relationship to be -1.75 (Figure S7), which is closer to the theoretical exponent of -2 as compared to -0.78 from a previous study.²¹ This result demonstrates that our as-grown Bi_2Se_3 films are of high quality and agree better with the theoretical model.²²

Figure 3d–f display the ARPES spectra of the Bi_2Se_3 films after the transfer using both 6 and 21.2 eV photons. Our 6 eV ARPES resolves clear electronic band structures from these millimeter-scale-transferred MBE-grown films. In these spectra, the TSS is preserved after the transfer for all three representative thicknesses. The LEC is out of the energy range of interest due to the reduced sample work function after the transfer (Figure S3). The TSS exhibits an overall higher electron doping after the transfer. This can be understood as the loss of selenium due to either its intrinsic volatility²⁴ or the chemical reaction of Bi_2Se_3 with H_2 ²⁵ or H_2O .^{26,27} The Lorentzian line widths of the TSSs extracted from the momentum distribution curves (MDCs) taken at E_F are listed in Table 1. The line widths from the post-transfer films are all less than 3 times the original line widths from the as-grown films. Given the direct exposure of the Bi_2Se_3 films to BOE, deionized water, and air, the amount of broadening is relatively low, particularly for the 5 QL film. This is in general consistent

with the previous Hall measurements on post-transfer Bi_2Se_3 films,¹⁸ which reported that the carrier mobilities from the post-transfer films can be comparable to or even higher than those from the pretransfer films. We emphasize that the quantitative connection between the MDC line width and the carrier mobility requires more intricate theoretical treatment due to the inequivalence of the spectroscopic scattering rate and the transport scattering rate.^{28,29} The QWSs are also preserved in the 6 eV ARPES spectra, yet the interband spacings ΔE_{n-0} are substantially modified, which is likely due to the change of the quantum well potential originated from the chemically induced surface and interface contamination (SI Note 6).

In contrast, the ARPES spectra on the post-transfer films taken with 21.2 eV photons exhibit poorly defined bands. On the 5 QL and 10 QL films (Figure 3e,f), some features corresponding to the QWSs may still be recognizable, but with a substantial momentum smearing. The TSSs are clearly absent. Importantly, based on the universal mean free path of photoelectrons,¹⁹ 6 eV photoemission has an effective probing depth of 3–4 nm, while 21.2 eV photoemission only detects the top 0.5 nm. The different surface sensitivities help rationalize the photon energy dependence: the more surface-sensitive 21.2 eV photoemission probes electrons primarily from the top QL which is significantly contaminated by O_2 , polymers, selenium, and other mechanisms; the more bulk-sensitive 6 eV photoemission additionally reveals the electronic structures from the inner layers. By traversing the diffuse valence bands in the 5 QL and 10 QL films resolved by 21.2 eV photons (Figure 3e,f), one can identify that the electronic structure for the surface layer is less electron-doped than that for the inner layers. This is consistent with the mechanism of electron-doping by the chemical reaction of Bi_2Se_3 and H_2O ,²⁶ as the surface layer will be least impacted by the solution during the peeling-off process (Figure 1d, Figure S8). Interestingly, the presence of the sharp TSSs in the 6 eV data indicates at least a partial wave function relocation of the TSS from the top QL to the second QL. This microscopic understanding is consistent with a time-resolved ARPES study on MnBi_4Te_7 , which unveiled a partial TSS wave function relocation due to the presence of surface defects,³⁰ but the effect is more drastic in the present case as a result of the heavy chemical processing. Moreover, we expect the TSS from the bottom QL to also undergo wave function relocation into the QL above it. The direct consequence of such wave function movements is an effective reduction of the number of QLs that comprise the TI (Figure 4), which is manifested in the opening of hybridization gaps in ultrathin films. Indeed, for the 3 QL film we observe a > 100 meV gap at the Dirac point after the transfer (Figure 3d), which is significantly enhanced from the ~ 60 meV hybridization gap below the Dirac point before the transfer (Figure 3a, Figure S3). We were unable to reliably extract the values of transfer-induced energy gaps from the 5 QL or 10 QL films (Figure 3e,f). Notably, no magnetic materials were used in the millimeter-scale transfer protocol, and therefore the magnetic impurities are unlikely to exist and cause the emerged Dirac gap. The transfer-induced gap can also be due to the hybridization between the TSS and a defect resonance state,³¹ but such a flat resonant state is not observed in our data for the 3 QL film (Figure 3d). Hence, we attribute the transfer-induced Dirac gap on the 3 QL film to the enhanced hybridization between the TSSs from the top and bottom layers due to the wave function relocation.

Table 1. Comparison of Lorentzian Line Widths of the Topological Surface States Extracted from the Momentum Distribution Curves Taken at E_F

thickness	fwhm as grown (\AA^{-1})	fwhm post-transfer (\AA^{-1})	ratio of broadening
3 QL	0.014	0.032	2.3
5 QL	0.013	0.023	1.8
10 QL	0.029	0.078	2.7

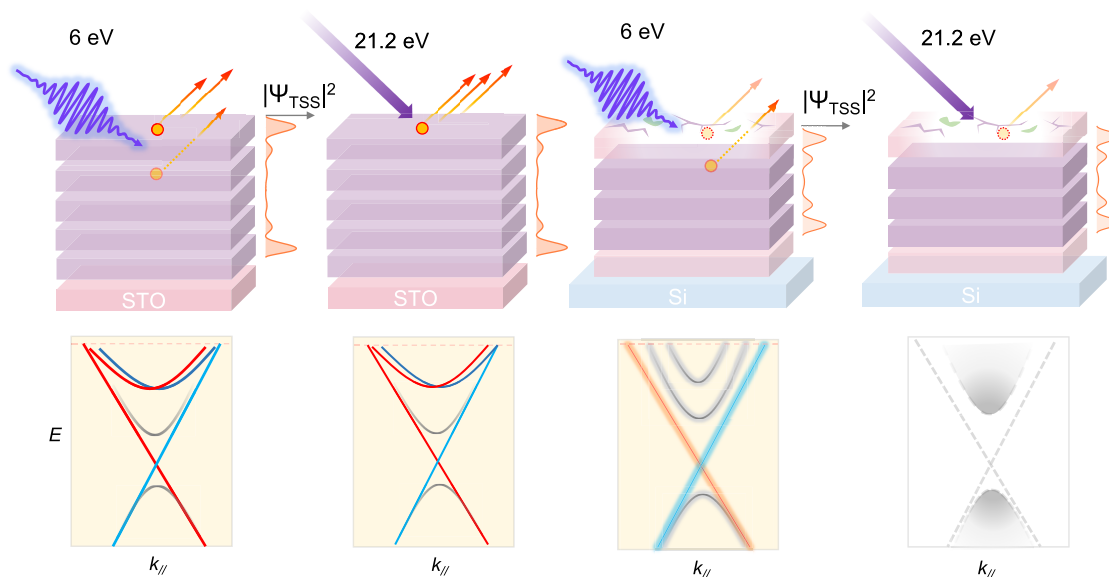


Figure 4. Wave function relocation due to transfer-induced contamination. Before the transfer, the topological surface state resides mostly in the outermost layers and can be probed by both the surface-sensitive 21.2 eV photoemission and the bulk-sensitive 6 eV photoemission. After the transfer, the surface layer is disordered by interacting with O₂, H₂O, polymer, and selenium, and the topological surface state is relocated partially into the inner layers. Only the 6 eV photoemission can detect the electronic structure.

The transferability of our Bi₂Se₃ films allows us to create suspended 10 QL membranes on top of a 5 μm silicon nitride aperture. Although electron diffraction does not reveal measurable strains on selected areas of 200 nm or larger (Figure S9), atomic-resolution scanning transmission electron microscopy (STEM) resolves as much as ±20% local strains concentrated near topological defects, which are formed before the transfer process and are consistent with previous studies on substrate-supported Bi₂Se₃ films³² (SI Note 7). An optical microscopy image is taken on a photonic hybrid system made by transferring a 6 QL Bi₂Se₃ film onto an array of photonic crystal cavities (Figure S10). With back lighting, this image highlights tearing lines which are separated by 5–20 μm. These results not only demonstrate the realistic constraints on the size of the devices incorporating the suspended Bi₂Se₃ membranes but also provide an explanation for our current inability to obtain ARPES results on these suspended membranes: additional oxidation and other channels of contamination can occur through the tears.

Our observation of the preservation of the TSS, together with the microscopic understanding of the TSS wave function relocation (Figure 4), provides an important physics foundation for the transferred ultrathin TI films. Even though wet-transfer methods^{16,18} have greatly enhanced our capabilities to build artificial heterostructures with MBE-grown films, the chemical processing leads to concerns about the preservation of the electronic structures, in particular the surface- and interface-related electronic states. Note that for ultrathin TI films, a significant disorder in the material can indeed lead to a topology change since the topology is sensitive to where the wave function is relocated.²² Therefore, it is far from trivial whether the TSS should be preserved in such a process. Our measurement, which reveals the preservation of the TSS for transferred Bi₂Se₃ films, lays the physics foundation for any future endeavors using the large-area transfer method for building heterostructures. Notably, this method can generally apply to other chalcogenide films grown

on oxide substrates. In SI Note 8, we demonstrate success in millimeter-scale liberation and ARPES characterization on Bi₂Te₃ thin films.

The microscopic understanding of the wave function relocation is also key to designing, rationalizing, and improving the functionalities of future TI-based devices. We note that the study pioneering the wet-transfer method for Bi₂Se₃ reported a trivial insulator behavior when tuning the chemical potential to the charge neutral point of a transferred 4 QL film,¹⁸ which disagrees with the theoretical prediction of a quantum spin Hall insulator phase.^{21,22} Applying our new understanding of the TSS wave function relocation, the effective number of layers comprising a TI after the transfer can be 3 or even smaller, which, according to the theoretical prediction,²² can potentially make the system a trivial insulator. We emphasize that this understanding of wave function relocation will be particularly important in future endeavors of building stacked or twisted TI heterostructures,^{33,34} since the formation of Moiré bands sensitively depends on the wave function overlap at the constructed interface. In addition to the transferred films, wave function relocation also needs to be considered in devices fabricated using processing methods that could potentially degrade the interface, such as spin–orbit torque devices³⁵ and TI-based Josephson junctions.³⁶

METHODS

Sample Growth. High-quality Bi₂Se₃ thin films were grown on 0.05 wt % Nb-doped SrTiO₃ (111) substrates by molecular beam epitaxy (MBE). The base pressure of the MBE chamber was 2×10^{-10} mbar. The SrTiO₃ (111) substrates were annealed at 1000 °C in the MBE chamber to obtain an atomically flat surface before growth. Selenium (99.999% purity) and bismuth (99.999% purity) were coevaporated onto the SrTiO₃ substrate from two effusion cells. The Bi₂Se₃ films were grown by using a two-step process.^{37,38} 1 QL Bi₂Se₃ was first grown at a low substrate temperature of 225 °C. The rest of the layers were grown at a higher temperature of 265 °C.

The amorphous Se capping layer was deposited *in situ* on the film at room temperature.

STEM Measurements. The atomic structural characterization was performed on an aberration-corrected scanning transmission electron microscope (STEM) by high-angle annular dark-field (HAADF) imaging using the aberration-corrected JEOL ARM200CF instrument at the University of Illinois at Chicago. The microscope was equipped with a cold field emission source operated at 200 kV. The HAADF detector angle was 90–270 mrad to give Z contrast images with a less than 0.8 Å spatial resolution. The 10 QL Bi₂Se₃ film was transferred on top of a silicon nitride TEM grid with 5 μm holes.

AFM and Raman Measurements. The AFM measurements were performed on a Bruker Multimode 8 AFM at the University of Chicago. The Raman measurements were performed at the University of Chicago on a HORIBA LabRAM Microscope with a laser source of 532 nm. A 6 QL Bi₂Se₃ film was transferred on top of a silicon nitride TEM grid with 5 μm holes. The Raman spectra were collected from the suspended Bi₂Se₃ film on the 5 μm aperture at 300 K.

ARPES Measurements. High-resolution ARPES measurements were carried out on the University of Chicago's Multi-Resolution Photoemission Spectroscopy platform which is connected to the MBE chamber. 205 nm photons were generated by frequency quadrupling of a Ti:sapphire oscillator with an 80 MHz repetition rate. The overall energy resolution was characterized to be better than 4 meV.³⁹ The laser spot size characterized by the full-width at half-maximum (fwhm) was around 10 μm.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.nanolett.4c00008>.

Layer-by-layer growth of Bi₂Se₃ films, AFM and Raman measurements of transferred Bi₂Se₃ films, low-energy cutoff in the ARPES spectrum measured by 6 eV, origins of the Dirac gaps in as-grown Bi₂Se₃ films, evolution of the quantum well states of Bi₂Se₃ films as a function of the film thickness, comparison of the quantum well states in Bi₂Se₃ films before and after the transfer, STEM characterization of suspended Bi₂Se₃ films, and preservation of topological surface states in millimeter-scale transferred Bi₂Te₃ films (PDF)

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Author Contributions

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Author Contributions

C.I.J.I., Q.G., K.D.N., C.Y., W.L., and S.Y. grew the Bi₂Se₃ thin films. C.I.J.I., Q.G., K.D.N., C.Y., W.L., H.R., and S.Y. prepared the exfoliated Bi₂Se₃ thin films. C.I.J.I., Q.G., K.D.N., C.Y., W.L. and S.Y. conducted the ARPES measurements. G.Y., T.S.M., M.Z., Y.S.M., and C.L. conducted the TEM measurements. K.D.N., C.I.J.I., E.H., and C.Y. conducted the AFM measurements. E.H. and C.L. conducted the Raman measurements. Q.G., K.D.N., C.I.J.I., and S.Y. wrote the manuscript with input from all authors. S.Y. conceived this project.

Notes

The authors declare no competing financial interest.

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