

# Fully gapped topological surface states in $\text{Bi}_2\text{Se}_3$ films induced by a *d*-wave high-temperature superconductor

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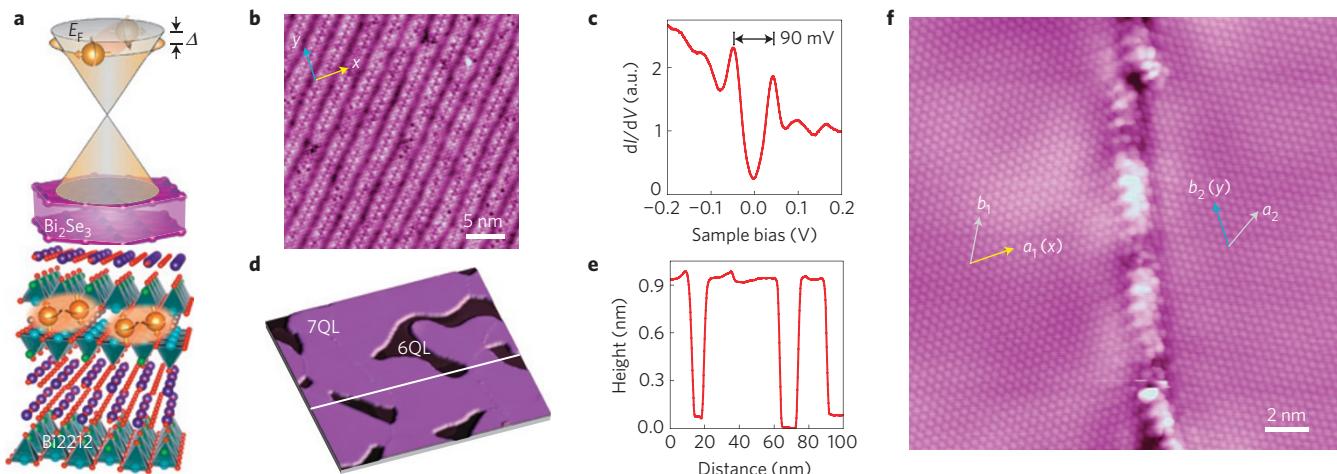
**Topological insulators are a new class of material<sup>1,2</sup>, that exhibit robust gapless surface states protected by time-reversal symmetry<sup>3,4</sup>. The interplay of such symmetry-protected topological surface states and symmetry-broken states (for example, superconductivity) provides a platform for exploring new quantum phenomena and functionalities, such as one-dimensional chiral or helical gapless Majorana fermions<sup>5</sup>, and Majorana zero modes<sup>6</sup> that may find application in fault-tolerant quantum computation<sup>7,8</sup>. Inducing superconductivity on the topological surface states is a prerequisite for their experimental realization<sup>1,2</sup>. Here, by growing high-quality topological insulator  $\text{Bi}_2\text{Se}_3$  films on a *d*-wave superconductor  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  using molecular beam epitaxy, we are able to induce high-temperature superconductivity on the surface states of  $\text{Bi}_2\text{Se}_3$  films with a large pairing gap up to 15 meV. Interestingly, distinct from the *d*-wave pairing of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ , the proximity-induced gap on the surface states is nearly isotropic and consistent with predominant *s*-wave pairing as revealed by angle-resolved photoemission spectroscopy. Our work could provide a critical step towards the realization of the long sought Majorana zero modes.**

The search for exotic quantum phenomena and new functionalities has been among the most tremendous driving forces for the fields of condensed-matter physics and materials science. Majorana zero modes, that is, Majorana fermions that are their own antiparticles and occur at exactly zero energy, are particularly fascinating not only because of their intriguing physics obeying robust non-Abelian statistics, but also owing to their potential application as building blocks for topological quantum computers<sup>7,8</sup>. Although significant progress has been made recently in one-dimensional semiconductor quantum wires coupled with conventional superconductors<sup>9–12</sup>, decisive evidence of Majorana zero modes has been lacking and many puzzles remain<sup>13</sup>. Topological insulators, whose hallmark is time-reversal-symmetry-protected surface states, may offer less restrictive experimental conditions for realizing Majorana zero modes<sup>1,2</sup>. Theoretically, Majorana zero modes are predicted to occur in vortex cores of three-dimensional topological insulators when they are in close proximity to conventional *s*-wave superconductors<sup>6</sup>; however,

identifying them experimentally has been challenging mainly because of the small pairing gap  $\Delta \sim 1$  meV induced by typical conventional superconductors<sup>14</sup> and the extremely small energy splitting  $\sim \Delta^2/\epsilon_F \sim 10^{-3}$  meV between Majorana zero modes and other low-lying vortex core bound states<sup>15</sup>, where  $\epsilon_F \sim 400$  meV is the typical Fermi energy of surface states<sup>14</sup>. A heterostructure between a topological insulator and a cuprate high-temperature superconductor (Fig. 1a), which has an order of magnitude enhancement in critical temperature  $T_c$  and  $\Delta$  compared with typical conventional *s*-wave superconductors, may offer a more feasible approach<sup>16,17</sup>.

To harbour Majorana zero modes with robust non-Abelian statistics, nodeless superconductivity needs to be induced on the surface states of topological insulators. Although previous tunnelling junction experiments have suggested a proximity-induced gap of 10 meV at the interface between exfoliated bulk  $\text{Bi}_2\text{Se}_3$  and  $\text{Bi}_2\text{Ca}_2\text{Cu}_2\text{O}_{8+\delta}$  (Bi2212) samples<sup>18</sup>, two critical questions remain unanswered for the proximity-induced superconductivity: whether the superconducting gap is induced on the surface states or on the bulk states, and what the pairing symmetry is. To address these issues and achieve high- $T_c$  superconductivity in topological insulators, we prepare high-quality  $\text{Bi}_2\text{Se}_3$  thin films directly on a freshly cleaved Bi2212 surface by molecular beam epitaxy (MBE). MBE growth can provide high-quality topological insulator films and controllable interfaces. More importantly, MBE films are suitable for ultrahigh vacuum measurements, such as scanning tunnelling microscopy (STM) and angle-resolved photoemission spectroscopy<sup>19</sup> (ARPES). The latter can be conveniently used to determine whether the gap is on the topological surface states or on the bulk bands, measure the gap size and reveal the pairing symmetry. Our ARPES measurements reveal a proximity-induced gap up to 15 meV, and this apparent gap is located only on the topological surface states with predominant *s*-wave pairing. One possible explanation for this unusual proximity effect is the combined consequence of disorder and the relative lattice orientation between cuprate and topological insulator film. Our work not only provides new opportunities for investigating the intriguing coupling between a topological insulator thin film and a *d*-wave superconductor, but also greatly expands the experimental range for realizing robust Majorana zero modes and achieving new functionalities.

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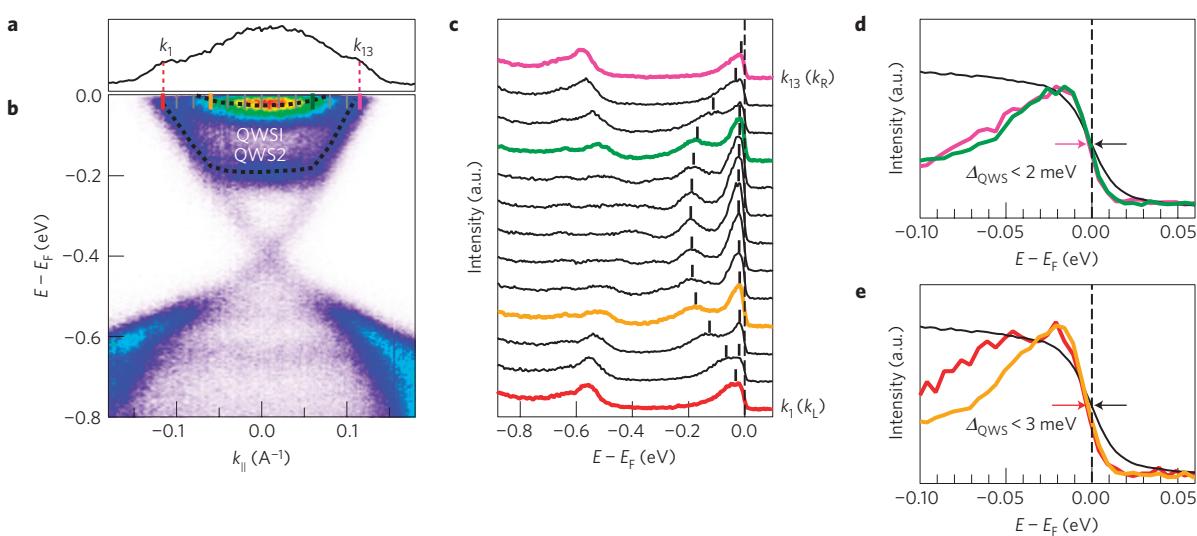
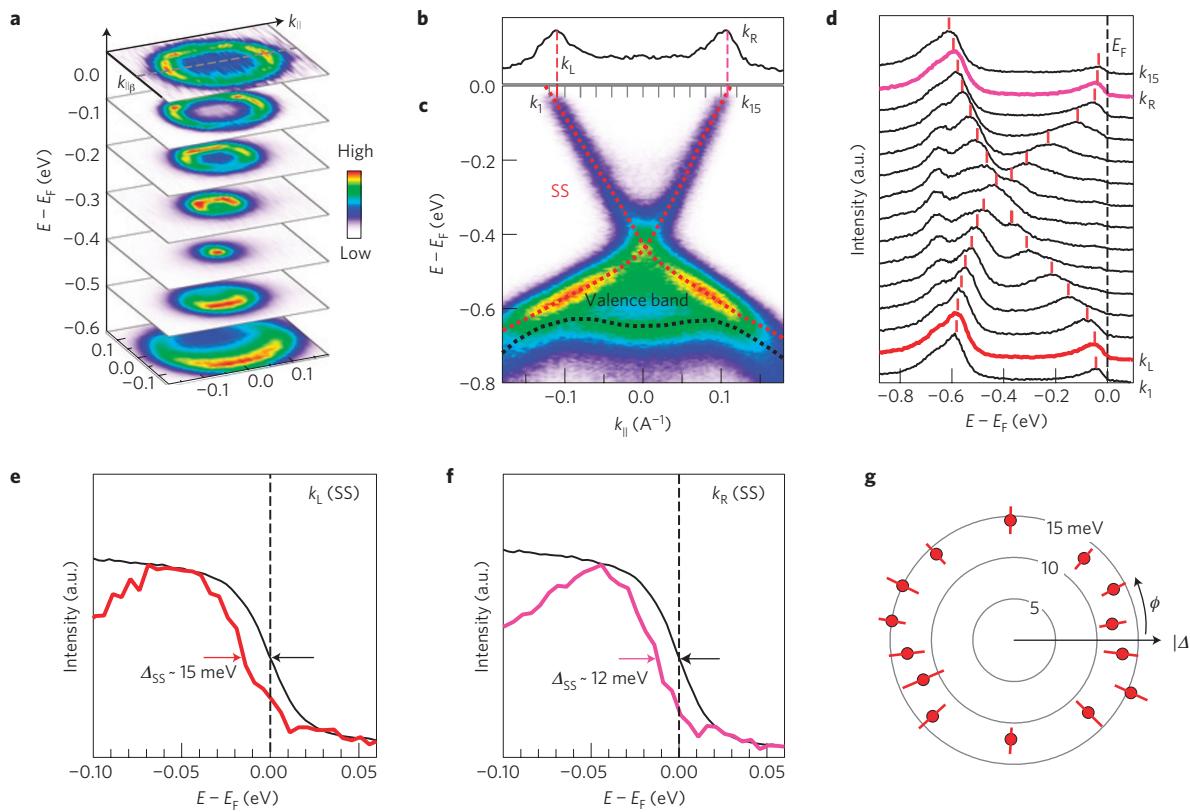
**Figure 1 | Schematic and characterization of the  $\text{Bi}_2\text{Se}_3/\text{Bi}2212$  heterostructure.** **a**, Schematic of the  $\text{Bi}_2\text{Se}_3/\text{Bi}2212$  heterostructure and proximity-induced gap on the surface states. **b**, STM topography (sample bias voltage 0.3 V, tunnelling current 0.03 nA) of the BiO surface. **c**, Typical  $d/dV$  spectrum showing a superconducting gap of 45 meV at 4.2 K on the surface of Bi2212. **d**, STM topography (100 nm  $\times$  100 nm, 1.0 V, 0.03 nA) of 7QL  $\text{Bi}_2\text{Se}_3$  films grown on Bi2212. **e**, Line profile along the white line in **d**. **f**, Atomic-resolved STM topography (0.4 mV, 0.07 nA) shows two predominant crystal orientations of  $\text{Bi}_2\text{Se}_3$ .

Figure 1a shows a schematic of the  $\text{Bi}_2\text{Se}_3/\text{Bi}2212$  heterostructure. STM topography (Fig. 1b) and scanning tunnelling spectroscopy (Fig. 1c) confirm the high surface quality and superconducting property of the cleaved Bi2212 sample. The growth of  $\text{Bi}_2\text{Se}_3$  thin films on Bi2212 is exceptionally challenging for two reasons: the low surface binding energy of Bi2212 prefers the island growth mode to the layer-by-layer mode; oxygen dopants in Bi2212 can easily oxidize the films grown on it when heated above 200 °C, a typical temperature for growing  $\text{Bi}_2\text{Se}_3$ . By carefully controlling the growth kinetics, we have succeeded in growing high-quality  $\text{Bi}_2\text{Se}_3/\text{Bi}2212$  heterostructures in the layer-by-layer growth mode so that high-resolution STM and ARPES measurements can be carried out. Figure 1d–f shows the high quality of the 7 quintuple layer (QL) thick  $\text{Bi}_2\text{Se}_3$  film on Bi2212. Although  $\text{Bi}_2\text{Se}_3$  and Bi2212 have very different (hexagonal versus tetragonal) crystal structures, the  $\text{Bi}_2\text{Se}_3$  films grown on Bi2212 show only two predominant crystal orientations with Se–Se bonds parallel to the  $x$  and  $y$  (anti-nodal, nearest Bi–Bi bond) directions of Bi2212, respectively (Fig. 1b,f and Supplementary Information).

The existence of topological surface states in the  $\text{Bi}_2\text{Se}_3/\text{Bi}2212$  heterostructure can be revealed in the ARPES data measured at 50 eV photon energy shown in Fig. 2. Near the Fermi energy ( $E_F$ ), the intensity map of the Dirac cone shows a circular shape, suggesting that the electronic structure is rather isotropic. The electron pocket decreases in size with binding energy and merges into a single point at  $-0.4$  eV (Fig. 2a). Figure 2c shows a cut through the  $\Gamma$  point. Here the conical dispersion is observed from  $E_F$  to  $-0.6$  eV, where the bulk valence bands start to arise. The electronic structure is in good agreement with the conical dispersion reported on the surface states in both bulk and thin film  $\text{Bi}_2\text{Se}_3$  samples<sup>14,20–22</sup>. The shift of chemical potential to 0.4 eV above the Dirac point is possibly attributed to charge transfer from the substrate and to defects in the  $\text{Bi}_2\text{Se}_3$  film. In addition to surface states and valence bands, bulk conduction bands, shown as quantum well-like states (QWSs) near the Fermi energy, are also expected in thin-film  $\text{Bi}_2\text{Se}_3$  samples<sup>14,22</sup>. However, the surface states and QWSs have different dipole matrix elements<sup>23</sup>, which makes it possible to separate their contributions by choosing an appropriate photon energy (Supplementary Information for detailed photon energy dependence). At 50 eV photon energy, the QWSs are strongly suppressed, thus allowing us to resolve the surface states without being affected by the bulk bands.

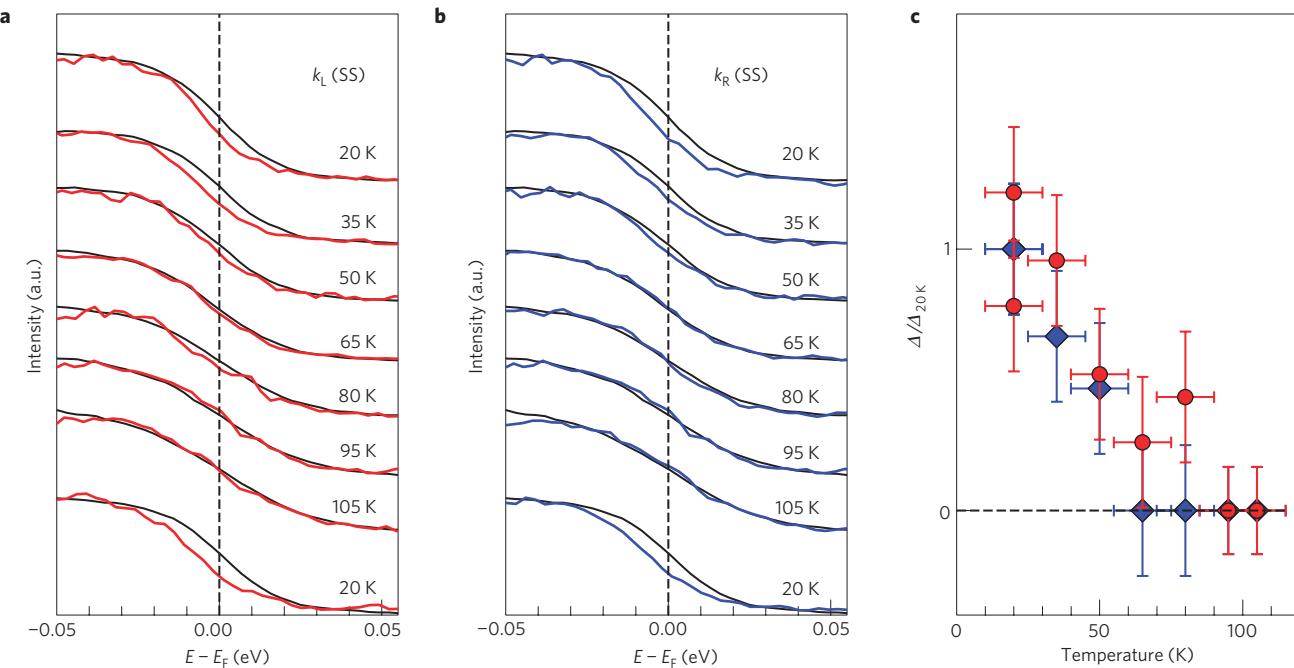
We analyse the energy distribution curves (EDCs) taken at a photon energy of 50 eV (Fig. 2d) to detect the proximity-induced gap on the surface states of  $\text{Bi}_2\text{Se}_3$ . The linear dispersions of the surface states can be observed in the EDCs, with peaks approaching the Fermi energy at two Fermi momenta  $k_L$  and  $k_R$ . We further zoom-in the EDCs at these two momentum positions (Fig. 2e,f). A comparison of the EDCs with a reference spectrum taken from a clean metal surface shows clearly that there is a suppression of intensity near  $E_F$ , that is, a gap is open. Following the standard ARPES procedure to extract the gap by the shift of leading edge position<sup>24</sup>, we obtain the gap size of 15 meV on the topologically protected surface states. We note that although this large gap can be observed only on films with extremely high quality (sharper ARPES peaks), a smaller gap of 6–8 meV is routinely observed in regular samples measured so far, which is still an order of magnitude larger than that induced by a conventional *s*-wave superconductor<sup>14</sup>. Surprisingly, despite the *d*-wave pairing of Bi2212 that is strongly anisotropic with four nodes of zero gap<sup>24</sup>, the induced gap on the surface states is rather isotropic (Fig. 2g) and consistent with *s*-wave pairing.

We examine the data taken at 20 K with photon energy of 30 eV where there is a strong intensity contribution from QWSs to determine whether a gap is induced on the bulk conduction bands. The strong intensity contribution from QWSs is evident in Fig. 3a–c. Here the lower QWS (labelled as QWS2) is clearly resolved to overlap with the surface states between  $E_F$  and  $-200$  meV with a nearly flat band bottom at  $-200$  meV. The inner QWS (labelled as QWS1) shows up as a smaller pocket near  $E_F$ . The EDCs at the Fermi momenta for QWS2 (pink and red curves) and QWS1 (orange and green curves) shown in Fig. 3d,e set an upper limit of 3 meV on the gap size for these QWSs. Data taken with other photon energies, for example 48 and 52 eV, where there are contributions from both the surface states and the QWSs, show that the gap size increases consistently with increasing contribution from the surface states (Supplementary Information). This observation further supports that the large gap does reside on the surface states and that the gap on the QWSs is significantly smaller. We note that the gap on the surface states is unlikely to be detected directly by STM measurements, because STM lacks the capability to distinguish surface states from bulk QWSs. Moreover, STM signals are dominated by QWSs that have negligibly small gap and yet have much higher density of states near the Fermi energy (for example, see the flatter band from QWS1 near  $E_F$ ).



The temperature-dependent ARPES data measured with 50 eV photon energy further reveal that the gap on the surface states is induced by superconductivity in Bi2212. Figure 4 shows EDCs at Fermi momenta measured at various temperatures on a sample with 7 meV gap. The gap is observed at least up to 50 K. Above 50 K, the gap becomes much harder to detect and completely vanishes at 100 K. To check reproducibility, we have subsequently cooled

down the sample from 110 K directly to 20 K and confirmed that the gap at 20 K was reproducible (bottom curves in Fig. 4a,b). Figure 4c shows the extracted gap size as a function of temperature. The similar temperature-dependent behaviour as the superconductivity transition for Bi2212 clearly suggests that the gap observed on the surface states of Bi<sub>2</sub>Se<sub>3</sub> is closely related to superconductivity in Bi2212 through the proximity effect.



**Figure 4 | Temperature dependence of the gap on the surface states measured with 50 eV photon energy.** **a,b,** EDCs at  $k_L$  and  $k_R$  (labelled in Fig. 2b) measured at different sample temperatures. Black curves were reference spectra for  $E_F$ . **c,** Extracted gap as a function of temperature. The gap values are normalized by the average gap size at 20 K. The gap is defined when the shifted EDC at  $k_L$  ( $k_R$ ) shows best overlap with the  $E_F$  reference spectrum, and the error bar is defined when the shifted EDCs starts to show clear deviation from the  $E_F$  reference spectrum.

The coupling between a  $d$ -wave superconductor and a topological insulator is an intriguing question. The observation of a nearly isotropic superconducting gap on the topological surface states and a much smaller gap on the bulk conduction bands is a reflection of such non-trivial coupling. If the crystalline group of the  $\text{Bi}_2\text{Se}_3$  film were tetragonal like Bi2212, the proximity-induced pairing gap in the  $\text{Bi}_2\text{Se}_3$  film would be expected to be nodal  $d$ -wave in the clean limit. However, because the  $\text{Bi}_2\text{Se}_3$  film possesses hexagonal crystal symmetry, the proximity-induced paring gap in the  $\text{Bi}_2\text{Se}_3$  is in principle a mixture of  $s$ -wave and  $d$ -wave. The  $s$ -wave component of the induced pairing in the  $\text{Bi}_2\text{Se}_3$  is zero when the nodal direction of Bi2212 lies in one of the reflection planes of the  $\text{Bi}_2\text{Se}_3$  for the following symmetry reasons. If this occurs, the hybrid  $\text{Bi}_2\text{Se}_3/\text{Bi}2212$  system would obey the reflection symmetry along the nodal direction. Under such reflection, the  $s$ -wave pairing in the  $\text{Bi}_2\text{Se}_3$  is even whereas the  $d$ -wave pairing in Bi2212 is odd. Fortunately, it is not the case for the  $\text{Bi}_2\text{Se}_3/\text{Bi}2212$  heterostructure here (Fig. 1b,f). Indeed, it turns out that the  $\text{Bi}_2\text{Se}_3$  reflection directions are at  $15^\circ$  or  $45^\circ$  from cuprate nodal directions (Supplementary Information); consequently, a sizable  $s$ -wave component is expected in the induced pairing of the topological insulator. Furthermore, because of the smaller gap and longer coherence length  $\xi \approx 2\hbar v_F/(\pi\Delta) \approx 14.4$  nm in  $\text{Bi}_2\text{Se}_3$  compared with cuprates ( $\approx 1$  nm), the  $d$ -wave gap is much more fragile against disorder and the formation of small domains; however, the  $s$ -wave gap is robust by Anderson's theorem<sup>25</sup>. Experimentally, we have observed that the pairing gap on the topological insulator's surface states is relatively large and nearly isotropic in the entire momentum space (Fig. 2g) although the pairing gap on the QWSs is negligible. A plausible explanation for this distinction is that the topological insulator's surface states have a predominant  $s$ -wave pairing gap that is robust against disorder as well as the formation of domains, whereas the bulk QWSs have a predominant  $d$ -wave pairing gap that is significantly suppressed by disorder. If the gap on the topological surface states of  $\text{Bi}_2\text{Se}_3$  is confirmed to be  $s$ -wave, this will open up a large range of experimental opportunities for observing and engineering a single

Majorana zero mode. For instance, STM measurements might be able to distinguish this single Majorana zero mode in a vortex core from other low-lying quasi-particle bound states because the energy splitting between them is of the order of  $\Delta^2/\epsilon_F \sim 0.5$  meV, which is within the energy resolution of the state-of-art STM. We note that non-Abelian statistics of the putative Majorana zero mode in a vortex core may not be sufficiently robust owing to the QWSs with vanishingly small gap. Tuning the chemical potential away from QWSs should avoid such complication from QWSs.

## Methods

The MBE growth and *in situ* STM experiments were conducted in an MBE–STM combined system with a base pressure of  $1.0 \times 10^{-10}$  Torr. Single-crystal Bi2212 samples with optimum oxygen doping ( $T_c \approx 91$  K) were grown by the travelling floating zone method<sup>26</sup>. The Bi2212 samples were cleaved in ultrahigh vacuum at room temperature, and annealed at  $250^\circ\text{C}$  for 3 h to degas the sample holder to avoid contamination of the film caused by outgassing of the sample holder during the growth process. The atomic structures of Bi atoms on the BiO-terminated surface of Bi2212 and the well-known supermodulation in the STM topographic image<sup>27</sup> (Fig. 1b) reveal the high quality of the cleaved surface. The characteristic V-shaped gap of 45 meV in the  $dI/dV$  spectrum in Fig. 1c confirms that the Bi2212 is still superconducting at near optimum doping and there is only a slight change in the oxygen doping after annealing (Supplementary Fig. S1).

$\text{Bi}_2\text{Se}_3$  films were then grown on Bi2212 at  $190^\circ\text{C}$  by co-evaporating Bi (99.999%) and Se (99.999%) from standard Knudsen cells under a Se-rich condition with a growth rate of approximately 0.07 QL per minute<sup>22</sup>. STM images were taken at  $4.2\text{ K}$  with a polycrystalline PtIr tip. The STM image in Fig. 1d shows an atomically flat  $\text{Bi}_2\text{Se}_3$  film on Bi2212 with a nominal thickness of 7 QL. Small regions of 6 QL are also present as indicated by the line profile in Fig. 1e. The step height of 0.95 nm is in agreement with the thickness of 1 QL  $\text{Bi}_2\text{Se}_3$  (ref. 28). The atomically resolved STM image (Fig. 1f) reveals a hexagonal lattice structure with a lattice constant of  $\approx 0.4$  nm, consistent with the Se-terminated (111) surface of  $\text{Bi}_2\text{Se}_3$  (ref. 28).

ARPES measurements were taken at BL12.0.1 of the Advanced Light Source at Lawrence Berkeley National Laboratory. Before being transferred from the STM chamber to the ARPES chamber, the samples were covered with an amorphous Se protection capping layer, which was removed in the ARPES chamber by annealing at  $200^\circ\text{C}$  for 30 min until sharp core levels (Supplementary Information) and clear dispersions were observed. The Fermi energy was calibrated by reference spectra taken from a clean metal (gold or tantalum) surface.

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## Author contributions

S.Z. and X.C. conceived and designed the experiments. H.D., Z.L., Y.-F.L., K.Z. and L.-G.Z. carried out MBE growth and STM measurements with assistance from S.-H.J., L.W., K.H., X.M., X.C. and Q.-K.X. Z.X., J.S., R.Z. and G.G. prepared the bulk Bi<sub>2</sub>Se<sub>3</sub> samples. E.W., W.Y., A.V.F. and S.Z. performed ARPES measurements and data analysis. S.Z., X.C., H.Y. and Q.-K.X. prepared the manuscript.

## Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at [www.nature.com/reprints](http://www.nature.com/reprints). Correspondence and requests for materials should be addressed to X.C. or S.Z.

## Competing financial interests

The authors declare no competing financial interests.