The Coexistence of Superconductivity and Topological Order in the Bi$_2$Se$_3$ Thin Films

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Three-dimensional topological insulators (TIs) are characterized by their nontrivial surface states, in which electrons have their spin locked at a right angle to their momentum under the protection of time-reversal symmetry. The topologically ordered phase in TIs does not break any symmetry. The interplay between topological order and symmetry breaking, such as that observed in superconductivity, can lead to new quantum phenomena and devices. We fabricated a superconducting TI/superconductor heterostructure by growing dibismuth triselenide (Bi$_2$Se$_3$) thin films on superconductor niobium diselenide substrate. Using scanning tunneling microscopy and angle-resolved photoemission spectroscopy, we observed the superconducting gap at the Bi$_2$Se$_3$ surface in the regime of Bi$_2$Se$_3$ film thickness where topological surface states form. This observation lays the groundwork for experimentally realizing Majorana fermions in condensed matter physics.

Shortly after the theoretical prediction and experimental discovery of topological insulators (TIs), such as HgTe quantum well and Bi-based materials (Bi$_{1-x}$Sb$_x$, Bi$_2$Se$_3$, and Bi$_2$Te$_3$) (1–11), the search for exotic quantum phenomena that were predicted to exist in TIs was under way (12–23). Unlike other ordered phases, TIs are characterized by a topological order that does not exhibit any symmetry breaking. The interplay between the topological order and symmetry breaking that appears in the or- dered phases of superconductors (SCs) and magnets may lead to many proposals of novel quantum phenomena such as the anomalous quantum Hall effect (23), time-reversal invariant topological superconductors (5), Majorana fermions (16, 17) and fault-tolerant quantum computation (24). However, experimentally it is very difficult to introduce these symmetry-breaking states into the TI’s surface. One proposal is to use the superconducting proximity effect (16, 17), either between a superconducting TI’s bulk and surface states or between an s-wave superconductor and a TI’s surface state. Bulk superconducting states were recently observed in Cu-intercalated Bi$_2$Se$_3$ (Cu$_x$Bi$_2$Se$_3$) and Bi$_2$Te$_3$ under high pressure (13–15). Cu$_x$Bi$_2$Se$_3$ retains the Dirac surface state, but its superconducting volume fraction is low (13, 14). It has also been shown that a supercurrent can flow through Bi$_2$Se$_3$ flakes or Bi$_2$Se$_3$ nanoribbons bordered by two superconducting electrodes (25, 26). Another way to realize the superconducting proximity effect between a TI and a SC is to grow TI/SC heterostructures, with an atomically sharp yet electronically transparent interface. This is a challenging task because of interface reaction and lattice mismatch between TI epilayers and available SC substrates. We have prepared atomically flat single-crystal Bi$_2$Se$_3$ thin films on 2H-NbSe$_2$(0001), an s-wave superconductor substrate, by molecular beam epitaxy (MBE). Using in situ scanning tunneling microscopy/spectroscopy (STM/STS) and angle-resolved photoemission spectroscopy (ARPES), we show that

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**Fig. 1.** Morphology of Bi$_2$Se$_3$ thin films grown on NbSe$_2$ substrate. (A) STM image of NbSe$_2$ (0001) surface with atomic resolution and CDW modulation. Bias voltage $V_s = 45$ mV. (B) Large-scale STM image of 2-QL Bi$_2$Se$_3$ film, $V_s = 200$ mV. Large-area 2 QL and small parts of 1 QL and 3 QL follow layer-by-layer growth mode. (C) Defined line profile along the line in (B) showing the height of each Bi$_2$Se$_3$ QL. All the step edges are sharp, indicating high-quality growth. (D) The Bi(110) layers are very smooth with large lateral size. The inset shows the atomic resolution of Bi films and moiré patterns, $V_s = 200$ mV. (E) Atomic-scale STM image of the Bi$_2$Se$_3$ film, with a structure similar to that of bulk crystals. (F) Schematics showing the layer-by-layer growth mode of Bi$_2$Se$_3$ thin films.
a superconducting gap is present at Bi$_2$Se$_3$ surface in the thickness regime where topological surface states form.

Figure 1A shows an atomically resolved STM topographic image of the cleaved NbSe$_2$(0001) surface, where an electronic modulation resulting from the presence of charge density waves (CDWs) is clearly observed. To grow atomically flat Bi$_2$Se$_3$ thin films, a Bi(110) bilayer (Fig. 1D and fig. S1) was first deposited on the NbSe$_2$ substrate. The Bi$_2$Se$_3$ thin films were then grown on the Bi(110) bilayer (27). Figure 1B shows a large-scale STM image of the atomically flat Bi$_2$Se$_3$ film with a nominal thickness of 2 quintuple layers (QL). The majority of the surface is covered by 2-QL films, but there are small areas with a thickness of 1 QL and 3 QL. The line profile (Fig. 1C) shows the thickness of different layers. Figure 1E reveals the hexagonal atomic lattice of top Se atoms with a spacing of 0.41 nm, implying that a well-defined (111) surface of Bi$_2$Se$_3$ is formed. The growth of Bi$_2$Se$_3$ films on Bi(110)-terminated NbSe$_2$ substrate proceeds in a typical layer-by-layer mode (Fig. 1F and fig. S2).

Local density of states (LDOS) can be obtained with STS by measuring differential conductance ($dI/dV$) spectra. On Bi$_2$Se$_3$ films, we observed superconducting gap-like spectra: a pronounced dip in the DOS at the Fermi level and peaks on both sides. Figure 2, A and B, shows the spectra measured on the Bi$_2$Se$_3$ films at a thickness of 3 QL and 6 QL, respectively. To exclude the possibility that the depression in the DOS at the Fermi level is a result of a zero-bias anomaly, we compare the STS data at 400 mK (lower panels of Fig. 2, A and B) to the data at 4.2 K (upper panels of Fig. 2, A and B) and find that sharp coherence peaks near ±1 meV are observed in both films. The results suggest that the Bi$_2$Se$_3$ films become superconducting due to the proximity effect of the NbSe$_2$ substrate. The superconducting transition is further supported by STS experiments under magnetic field, applied to the sample in the surface-normal direction. Figure 2C shows a series of $dI/dV$ spectra that were obtained after averaging over a large area of film in different applied fields. The shape of the spectra changes as the magnetic field increases: The zero-bias conductance increases with the magnetic field, and the coherence peaks on both sides of the gap diminish, consistent with the formation of superconducting states in Bi$_2$Se$_3$ films. The energy gap closes at about 7 K (fig. S3). We find that the Bi(110) bilayer has very little effect on the electronic states of NbSe$_2$ (fig. S4). Because the intercalated Bi(110) bilayer is very thin (0.6 nm), Bi$_2$Se$_3$ films show smaller coherence peaks and finite (although small) zero-bias differential conductance. This observation is also consistent with the scenario of the SC proximity effect; the Cooper pair potential decreases with the increasing normal metal thickness. The evolution of the superconductivity is shown in Fig. 3A, from which one can see that the energy gap at the Fermi level changes dramatically as the film thickness increases. We use both the Bardeen-Cooper-Schrieffer (BCS)–like tunneling spectrum function and the simple proximity effect function [equation 5.3 in (29)] to fit the spectra. The upper panel of Fig. 3B displays the STS spectrum of pure NbSe$_2$ at 4.2 K that fits the BCS-type function very well. A superconducting gap of 1.1 ± 0.1 meV is obtained. For a 3-QL film (Fig. 3B, lower panel), neither of the fits is very good, although they roughly give similar gap size. The exact description of the STS curves may require further theoretical inputs. Nevertheless, we plot the fitting results in Fig. 3C. The decrease of the energy gap is qualitatively in agreement with the theoretical description for the proximity effect.

We now show that the topologically ordered surface states persist despite the formation of the
superconducting gap in the Bi₂Se₃ films. Bulk topological insulator Bi₂Se₃ has a spin nondegenerate Dirac cone around the Γ point. For a slab of Bi₂Se₃, however, the boundary states from two opposite surfaces may be coupled by quantum tunneling so that a gap opens up and the massless Dirac point disappears subsequently. The crossover thickness where a Dirac cone forms depends on the interface of TI films and substrates. For example, in the case of Bi₂Se₃/SiC films (10) with a very sharp interface, the crossover thickness is 6 QL. In our work, the Dirac point is also clearly observed on 6-QL films, implying that our interface is very sharp, which is consistent with our STM results (Fig. 1). Figure 4 shows the experimental energy band dispersions of the Bi₂Se₃ thin films at different thicknesses measured with ARPES. There is an energy gap at the binding energy of 0.6 eV on the ARPES spectra when the film thickness is 3 QL. Compared with the electronic states of an intrinsic Bi₂Se₃ crystal, the Fermi level of the 3-QL sample is shifted upward as a result of possible charge transfer from the Bi(110) bilayer and substrate. Quantum-well-like states (labeled as QW in Fig. 4) were also observed in our system. The charge transfer generates a large gradient of electric field that enhances the Rashba-type spin-orbit coupling. The energy band splitting resulting from spin-orbital coupling is observed at a binding energy of ~0.15 eV (Fig. 4A). When the film thickness is increased to 6 QL, the gap disappears and the Dirac point (labeled as DP in Fig. 4) emerges at ~0.45 eV below Fermi level, indicating decoupling of the interface and surface (Fig. 4B). The quantum-well-like bands within the Dirac cone do not show spin-orbital splitting, which indicates that the electric field becomes weak on the surface of 6-QL films. Dirac points are also observed in the films with a thickness of 9 QL and 12 QL.

Our observation of the coexistence of the superconducting gap and topological surface states in the surface (interface) of Bi₂Se₃ thin films makes this TI/SC heterostructure very useful for understanding the unusual properties of superconductivity with topological order. One immediate possible outcome will be the detection of Majorana fermions (MFs). Non-Abelian MFs may emerge as zero-energy core states in a vortex (16–22) on the Bi₂Se₃ surface (interface). Early theoretical proposals for detecting MFs require a superconducting overlap, which, however, prevents experimental probing of vortices on the topological surface. In our geometry, topological surface states on the superconductor substrate have a great advantage in that the Majorana-bound states can be directly probed in the surface vortex core. There are two independent surface states in the film when the film thickness is greater than 6 QL. One is the lower surface or TI/SC interface; another is the upper surface or TI/vacuum interface. On both surfaces, non-Abelian MFs may emerge as vortex core states. Although the Fermi level is not in the bulk band gap, our SC Bi₂Se₃ films (>6 QL) are analogous to the weakly doped superconducting three-dimensional TI films as proposed in (12, 22). The bulk continuum states acquire a proximity-induced gap, and this leaves open the possibility of observing spatially separated Majorana zero modes on the top surface (22). It is also possible that in our system, the top gate can be applied on the surface to tune the Fermi level to the bulk band gap and, hence, single Majorana zero mode can exist in the Bi₂Se₃/NbSe₂ interface. In thin TI films (<6 QL), the Majorana zero modes from the upper and lower surfaces could couple with each other and open up a finite energy gap. In this case, one could introduce magnetic elements into the thin TI film so that a quantum anomalous Hall state is obtained. The proximity effect between the NbSe₂ superconductor and the thin magnetic TI film may give rise to a (p + ip)-wave pairing state and a single Majorana zero mode (30).

References and Notes
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27. Materials and methods, including details of sample characterization and the influence of Bi(110) and temperature dependence, are available as supporting material on Science Online.

Fig. 4. Energy-band dispersion measurements from ARPES of the Bi₂Se₃ thin films. QW-like states are observed on all thin films. (A) In the 3-QL film, an energy gap resulting from the coupling between the lower and upper surfaces was observed. Rashba-type spin-orbital splitting of QW was observed (white arrow). The spectra were taken using He-l 21.2 eV photon. (B) At 6 QL DP at the binding energy of ~0.45 eV recovers. Surface states (SS) form a Dirac cone. The spectra were taken using 36 eV photon. (C) 9 QL (D) 12 QL.
A 2D Quantum Walk Simulation of Two-Particle Dynamics

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Multidimensional quantum walks can exhibit highly nontrivial topological structure, providing a powerful tool for simulating quantum information and transport systems. We present a flexible implementation of a two-dimensional (2D) optical quantum walk on a lattice, demonstrating a scalable quantum walk on a nontrivial graph structure. We realized a coherent quantum walk over 12 steps and 169 positions by using an optical fiber network. With our broad spectrum of quantum coins, we were able to simulate the creation of entanglement in bipartite systems with conditioned interactions. Introducing dynamic control allowed for the investigation of effects such as strong nonlinearities or two-particle scattering. Our results illustrate the potential of quantum walks as a route for simulating and understanding complex quantum systems.

Quantum simulation constitutes a paradigm for developing our understanding of quantum mechanical systems. A current challenge is to find schemes that can be readily implemented in the laboratory to provide insights into complex quantum phenomena. Quantum walks (1, 2) serve as an ideal test bed for studying the dynamics of such systems. Examples include understanding the role of entanglement and interactions between quantum particles, the occurrence of localization effects (3), topological phases (4), energy transport in photosynthesis (5, 6), and the mimicking of the formation of molecular states (7). Although theoretical investigations already take advantage of complex graph structures in higher dimensions, experimental implementations are still limited by the required physical resources.

All demonstrated quantum walks have so far been restricted to evolution in one dimension. They have been realized in a variety of architectures, including photonic (8–11) and atomic (12–14) systems. Achieving increased dimensionality in a quantum walk (15) is of practical interest because many physical phenomena cannot be simulated with a single walker in a one-dimensional (1D) quantum walk, such as multiparticle entanglement and nonlinear interactions. Furthermore, in quantum computation based on quantum walks (16, 17), search algorithms exhibit a speed-up only in higher dimensional graphs (18–20). The first optical approaches to increasing the complexity of a linear quantum walk (21, 22) showed that the dimensionality of the system is effectively expanded by using two walkers, keeping the graph one-dimensional. Although adding additional walkers to the system is promising, introducing conditioned interactions and, in particular, controlled nonlinear interactions at the single-photon level is technologically very challenging. Interactions between walkers typically result in the appearance of entanglement and have been shown to improve certain applications, such as the graph isomorphism problem (23). In the absence of such interactions, the two walkers remain effectively independent, which severely limits observable quantum phenomena.

We present a highly scalable implementation of an optical quantum walk on two spatial dimensions for quantum simulation, using frugal physical resources. One major advance of a 2D system is the possibility to simulate a discrete evolution of two particles, including controlled interactions. In particular, one walker, in our case a coherent light pulse, on a 2D lattice is topologically equivalent to two walkers acting on a 1D graph. Thus, despite using an entirely classical light source, our experiment is able to demonstrate several archetypal two-particle quantum features. For our simulations, we explored the similarity between coherent processes in quantum mechanics and classical optics (24, 25), as it was used, for example, to demonstrate Grover’s quantum search algorithm (26).

A quantum walk consists of a walker, such as a photon or an atom, which coherently propagates between discrete vertices on a graph. A walker is defined as a bipartite system consisting of a position (x) and a quantum coin (c). The position value indicates at which vertex in the graph the walker resides, whereas the coin is an ancillary quantum state determining the direction of the walker at the next step. In a 2D quantum walk, the basis states of a walker are of the form |x1, x2, c1, c2⟩ describing its position x1,2 in spatial dimensions one and two and the corresponding two-sided coin parameters with c1,2 = ±1. The evolution takes place in discrete steps, each of which has two stages, defined by coin (C) and step (S) operators. The coin operator coherently manipulates the coin parameter, leaving the position unchanged, whereas the step operator updates the position according to the new coin value. Explicitly, with a so-called Hadamard (H) coin C1 = H1 ⊗ H2, a single step in the evolution is defined by the operators:

\[ H_1 |x_1, \pm 1\rangle \rightarrow (|x_1, 1\rangle \pm |x_1, -1\rangle) / \sqrt{2}, \forall y_i = 1, 2 \]

\[ S_1 |x_1, x_2, c_1, c_2\rangle \rightarrow |x_1 + c_1, x_2 + c_2, c_1, c_2\rangle \] (1)

The evolution of the system proceeds by repeatedly applying coin and step operators on the initial state |ψn⟩, resulting in |ψn⟩ = (SC) |ψn⟩ after n steps. The step operator S hereby translates superpositions and entanglement between the coin parameters directly to the spatial domain, imprinting signatures of quantum effects in the final probability distribution.

We performed 2D quantum walks with photons obtained from attenuated laser pulses. The two internal coin states are represented by two polarization modes (horizontal and vertical) in two different spatial modes (27), similar to the proposal in (28). Incident photons follow, depending on their polarization, four different paths in a fiber network (Fig. 1A). The four paths correspond to the four different directions a walker...
Supporting Online Material for

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Materials and Methods

STM and ARPES experiments were carried out in two UHV systems, one is equipped with 400 mK STM and MBE, another with STM, MBE and ARPES. The base pressures of the systems are better than $2 \times 10^{-10}$ Torr. The superconductive 2H-NbSe$_2$ crystals were made by vapor transport method. NbSe$_2$ has a layered sandwich structure (Se-Nb-Se) along the $<0001>$ direction that consists of two hexagonal Se sheets with an intercalated Nb sheet connected together through weak Van der Waals bonds. NbSe$_2$ crystals were cleaved in situ at room temperature resulting in shiny flat (0001) surfaces. Its STM images show atomically flat terraces that extend to several hundreds of nanometers. The charge dynamics of 2H-NbSe$_2$ below Tc (7.2K) has been studied extensively using STM. Bilayer Bi(110) films were first prepared on the NbSe$_2$(0001) substrates. High-quality Bi$_2$Se$_3$ films were grown thereon by co-evaporating Bi and Se sources at a substrate temperature of about 200 °C. Bi (99.9999%) and Se (99.999%) were both evaporated from standard Knudsen cells. The typical growth rate of Bi$_2$Se$_3$ thin films was about 1/3 QL per minute. The film growth was monitored in situ by reflection high energy electron diffraction (RHEED). To further improve the film quality, post-growth annealing was carried out in Se molecular beam. The STM measurements were carried out in an USM-1300S3HE (Unisoku) STM system. All STM topography images are taken at 4.2 K with I = 0.1 nA. The dI/dV data of superconducting gaps were obtained via lock-in technique with modulation signal voltage 0.1 mV with a frequency of 991 Hz. ARPES measurements were performed at 90K and 15K using He-I$\alpha$ light (21.2 eV) in the lab and 28-60 eV photons at Advanced Light Source (ALS) beam lines 12.0.1 with VG Scienta analyzer. Energy resolution was set to 20meV.

Supplementary Text

The structure of the ultrathin wetting layer

The lattice constant of 2H-NbSe$_2$(0001) surface is 0.35nm and the lattice constant of Bi$_2$Se$_3$ (111) surface is 0.413nm, leading to a huge lattice mismatch ~ 18%. In order to obtain high quality atomically flat thin Bi$_2$Se$_3$ films, we found that preparation of one Bi(110) bilayer (BL) as a wetting layer (0.6nm) on NbSe$_2$ substrate is necessary. Figure S1A shows the atomic resolution STM topography of 1 BL Bi(110) film. A rectangular unit cell (Fig. S1A) with $a = 4.74$ Å and $b = 4.54$ Å can be identified in the image which is consistent with the lattice structure of Bi(110) surface (31). The arrow indicates the Bi[1-10] crystal orientation. Figure S1B shows the top view of atomic configuration of Bi(110) surface. The surface unit cell contains two atoms. The central atom in the cell is offset to the short edge of the unit cell to reveal zigzag chains structure (32). Bright Moiré patterns (Fig. S1A) with hexagonal symmetry can also be seen due to lattice mismatch between the NbSe$_2$ substrate and the epitaxial Bi film.

Figure S2 presents the RHEED pattern of NbSe$_2$ substrate and the 12 QL Bi$_2$Se$_3$ films. The line-like RHEED pattern suggests that the Bi$_2$Se$_3$ film is flat. The qualities of the films were discussed in the main text.

Temperature dependence of the superconducting gap induced by proximity effect
Figure S3 presents the temperature dependence of the energy gap of 3 QL Bi$_2$Se$_3$ films. With increasing temperature, the gap fades away gradually. Tc for 3QL is between 6 K and 7 K. Since the superconductivity in Bi$_2$Se$_3$ is from proximity effect, Tc should be only dependent on the NbSe$_2$.

**Influence of Bi(110) bilayer on the electronic structure of NbSe$_2$**

From ARPES experiments, we found that the Bi(110) bilayer has very little effect on the electronic states of NbSe$_2$. Fig. S4A shows the Fermi surface of 1 BL Bi(110) grown on NbSe$_2$ substrate overlaid with the Fermi surface (green dashed line) of bare NbSe$_2$ from previous experiment(33). Surprisingly, although covered with 1 BL of Bi, the measured Fermi surface is nearly the same as that of NbSe$_2$. There is little spectra weights from Bi(110). Fig. S3B shows the band dispersion along the direction marked in Fig. S3A. Besides the strong hole-like bands from NbSe$_2$, no other sharp features were observed. Near the $\Gamma$ point, there are very weak hole like bands which may come from Bi(110) BL (34).
Fig. S1

(A) Atomic resolution STM topography of 1 BL Bi(110) film grown on 2H-NbSe$_2$(0001) substrate. $V_s = 1$ V, $I_s = 100$ pA. The Bi[1-10] crystal orientation is indicated by the white arrow. The black rectangle presents the unit cell. Large hexagon indicates the Moiré pattern. (B) Top view of the atomic configuration of Bi(110) surface. Rectangular unit cell contains two Bi atoms with lattice constants $a = 4.74$ Å and $b = 4.54$ Å. The black arrow indicates the Bi[110] crystal orientation.
Fig. S2
RHEED patterns (A) NbSe$_2$(0001) substrate. Well-ordered and flat surface was obtained after cleavage in UHV at room temperature. (B) 12 QL Bi$_2$Se$_3$ films in two-dimensional growth mode.
Fig. S3
Temperature dependence of the energy gap of 3 QL Bi$_2$Se$_3$/NbSe$_2$. 
Fig. S4
Electronic structure of 1BL Bi(110)/NbSe₂. (A) ARPES intensity map near Fermi level (±5 meV). The dashed line (green) was the Fermi surface of NbSe₂(0001) from previous experimental data obtained from Ref. (33). The white dashed lines show the Γ-M and Γ-K directions. The measured Fermi surface matches that of NbSe₂(0001) very well. (B) Electronic band dispersion crossing the Γ points along the directions as marked (yellow dashed line) in panel (A) Besides strong hole like bands from NbSe₂, there are some weak hole-like bands near Γ points which may come from Bi(110).
References


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27. Materials and methods, including details of sample characterization, influence of Bi(110) and temperature dependence are available as supporting material on Science Online.


