Patterning Superconductivity in a Topological Insulator

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ABSTRACT: Topologically protected states in combination with superconductivity hold great promise for quantum computing applications, but the progress on electrical transport measurements in such systems has been impeded by the difficulty of fabricating devices with reliable electrical contacts. We find that superconductivity can be patterned directly into Bi²Se³ nanostructures by local doping with palladium. Superconducting regions are defined by depositing palladium on top of the nanostructures using electron beam lithography followed by in situ annealing. Electrical transport measurements at low temperatures show either partial or full superconducting transition, depending on the doping conditions. Structural characterization techniques indicate that palladium remains localized in the targeted areas, making it possible to pattern superconducting circuits of arbitrary shapes in this topological material.

KEYWORDS: topological insulators, patterning, superconductivity, electron transport, transmission electron microscopy, Raman spectroscopy

Topological superconductors are predicted to host Majorana fermions,¹,² which may be used as building blocks for fault-tolerant quantum computing.³,⁴ Whereas some evidence of topological superconductivity has been found in doped bulk topological insulators⁵−¹¹ and Majorana fermions have been reported in one-dimensional systems in proximity to superconductors,¹²−¹⁵ one of the remaining challenges is to find a convenient experimental platform for realizing circuits that would allow a pairwise exchange of Majorana fermions known as braiding.⁴

Bi²Se³ is a widely studied topological insulator¹⁶ that is known to become superconducting upon doping with copper or other metallic elements.⁵,⁸,¹⁰ The bulk Cu-doped Bi²Se³ was predicted to have topological properties,¹⁷ which have been reported in some experiments,⁹−¹¹ whereas others indicated conventional superconductivity.¹⁸,¹⁹ It has been shown that the stability and the properties of this material depend critically on growth and quenching conditions.²⁰ An alternative to bulk doping is to induce superconductivity on the surface of Bi²Se³ by proximity to a conventional superconductor.²¹−²⁴ Whereas both the bulk-doped and proximity-coupled systems are convenient platforms for studying topological superconductivity by spectroscopic methods, harnessing their topological properties will require transport measurements, which remain to be a challenge due to the difficult device architecture and poor electrical contacts.

Some of these issues could be effectively resolved by combining the above approaches in order to create native superconducting and normal regions in desired patterns within the crystal of a topological insulator. Here, we show that superconductivity can be patterned directly into a topological insulator Bi²Se³ by doping selected regions with palladium (Pd), using electron beam lithography and in situ annealing. Electrical transport measurements at low temperatures show superconducting transitions in the doped regions, whereas structural characterization techniques indicate that Pd remains localized in the targeted areas. By providing superconductivity in desired locations with clean interfaces, this will lend itself to patterning devices and enable the transport measurements that are needed for applications.

RESULTS AND DISCUSSION

Bi²Se³ nanocrystals of thickness between 70 and 100 nm were mechanically exfoliated onto Si substrates. Pd leads were patterned and deposited onto the nanocrystals using standard...
electron beam and optical lithography methods. Bi₂Se₃ devices with Pd leads were metallic down to 0.25 K, and neither pure palladium nor Bi₂Se₃ is superconducting on their own. The devices were annealed at a temperature between 200 and 300 °C. An optical image of a device that was annealed at 220 °C for 1 h is shown in Figure 1a. After being annealed, the 100 nm thick Pd leads are no longer visible by atomic force microscope measurements on top of Bi₂Se₃, while still showing the 100 nm thickness everywhere else. We show below that the Pd is absorbed by the Bi₂Se₃ crystal during annealing. A second layer of palladium leads was added over the doped areas in order to ensure good contact for electrical measurements. After being annealed, the devices showed a superconducting transition around 0.8 K, as shown in Figure 1.

Figure 1. Electrical measurements of a Pd-doped Bi₂Se₃ device after annealing. (a) Optical microscope image of a sample after annealing under flowing Ar gas at 220 °C for 1 h. The irregular shape in the center is an exfoliated Bi₂Se₃ flake, and the Pd leads are marked by numbers 1−6. The parts of the Bi₂Se₃ flake that had been covered with 90 nm of Pd appear darker in the image. (b) Four-probe resistance as a function of temperature with current sourced across leads 1 and 6 and voltage measured across leads 2 and 3. A transition to a lower resistance state is observed around 800 mK. (c) Four-probe V−I curve with current sourced from leads 1 to 6 and voltage measured across leads 2 and 5. (d) Four-probe differential resistance measurements with current sourced from lead 1 to 6 and voltage measured across leads 2 and 5 (red), leads 2 and 3 (green, region 1), leads 3 and 4 (blue, region 2), and leads 4 and 5 (purple, region 3). All three regions show transitions but at slightly different bias currents. Differential resistance measurements of the whole device, with voltage measured across 2 and 5, are shown as a function of magnetic field (e) and temperature (f). In both sets of data, two primary peaks are observed at 2.5 and 3.5 μA.

Figure 2. Images and EDS spectra of exfoliated Bi₂Se₃ flakes before and after thermal annealing. (a) Optical image of Bi₂Se₃ flakes exfoliated onto a silicon nitride window and covered with lines of palladium. (b) TEM image of a flake with a palladium line, circled in red in (a). (c) EDS spectra of red circled area in (b) showing composition of Bi₂Se₃ and signal from the silicon nitride window. (d) Optical image of flakes shown in (a) after thermal annealing for 1 h at 295 °C under argon gas flowing at 200 sccm. (e) TEM image of a flake, circled in red in (d), post-annealing. (f) EDS spectra, from location circled in red in (e), post-annealing, indicating that palladium has entered into the flake.
peaks are observed at 2.5 and 3.5 critical temperatures, which is typical for superconducting samples with a critical temperature of 2.5 K. As we will show below, the resistance below the transition is caused by a section of the crystal between the leads, which remains undoped. The current-voltage measurement across the entire device, with current sourced between leads 1 and 6 and voltage measured across leads 2 and 5, is shown in Figure 1e,f, respectively. As either the temperature or magnetic field is increased, the dip in resistivity at low currents gradually decreases until a steady-state concentration is reached.

Temperature and magnetic field dependence of the differential resistance across the entire device is shown in Figure 1c, respectively. As either the temperature or magnetic field is increased, the dip in resistivity at low currents gradually disappears, which is typical for superconducting samples with a critical temperature of about 2.5 K. In both sets of data, two primary peaks are observed at 2.5 and 3.5 μA. A similar behavior of dV/dI has been reported previously in Bi2Se3 samples in which the Pd has spread into the Bi2Se3 crystal between the leads, which remains undoped. The resistance below the transition is caused by a section of the sample that is superconducting. As we will show below, the Pd has spread into the Bi2Se3 flake provided by the EDS spectrum from the same region as Figure 2c, which now includes a peak indicating the presence of Pd along with the original Bi, Se, and Si peaks.

In order to better understand the dynamics and the extent of Pd migration in the Bi2Se3 flake, EDS maps of the flake shown in Figure 2 was acquired after annealing, as shown in Figure 3. The elemental spatial maps show that Bi (Figure 3b) and Se (Figure 3c) peaks were present across the entire flake, and the Pd (Figure 3d) extended only up to a certain length into the flake from the leads, leaving the central region an unaltered Bi2Se3 flake. The weaker peak intensity of Pd at the lead-substrate interface compared to lead-substrate interface and the uniform atomic ratio of Pd inside the flake suggest that the Pd atoms move from the leads into the flake during annealing until a steady-state concentration is reached.

In Figure 3e, the atomic ratios of Bi/Se, Pd/Bi, and Pd/Se were calculated along a line profile (point scan area = 0.04 μm2), as shown in Figure 3e. The ratios of Pd/Bi and Pd/Se were both seen to have a valley in the central region as expected due to the absence of Pd, consistent with the EDS Pd map. It was seen that the Bi/Se atomic ratio remained approximately constant throughout at a value slightly greater than 0.7 or 2:3; that is, the Se concentration was lower than expected, indicating that some loss occurred as a result of the annealing process. While Bi2Se3 typically shows metallic properties in the bulk due to Se vacancies, these properties can be controlled by growth methods,25 chemical doping,26 or electrostatic doping.26

To further investigate the motion of Pd inside Bi2Se3, electron diffraction was studied in three different regions, specified in Figure 4a. Region 1 is an unaltered Bi2Se3 region, whereas regions 2 and 3 did not contain Pd before annealing. The diffraction in region 1 (Figure 4b) shows the normal hexagonal Bi2Se3 radial pattern for the [1120] direction, with a calculated lattice parameter value of a = 0.413 nm.

A distorted polycrystalline lattice structure was obtained for regions 2 and 3, shown in Figure 4c,d, respectively. The
constant Bi/Se atomic ratio and the presence of a polycrystal-
line diffraction pattern in regions 2 and 3 suggest that Pd is
interrupting the host crystal structure without altering the relative
concentration of Bi and Se atoms. Further in-depth material
characterization is required for better understanding and tuning
the Pd migration in Bi$_2$Se$_3$.

Overall, the TEM analysis of the annealed
flake shows that the Pd is absorbed by the Bi$_2$Se$_3$
flake during the annealing
process and that the absorption occurs uniformly with a leading
edge across the flake. Although superconductivity has been
reported before in several compounds containing Pd and Bi or
Se, transport data and the TEM analysis do not show that
such compounds are forming in our samples.

By comparing optical images and EDS data, we see that the
regions penetrated by Pd appear gray on the optical images,
providing a simple way to optically locate the Pd. Comparing
samples annealed at different temperatures, we find that the
extent of the Pd spreading can be controlled by the annealing
temperature. At lower annealing temperatures, Pd is absorbed
only in the targeted areas (as in Figure 1 and Figure 5), whereas
at higher annealing temperatures, it also spreads away from the
targeted areas (as in Figure 3). Additional measurements taken
over several weeks indicate that the samples do not degrade
with time, and the Pd remains in place.

Further evidence that the Bi$_2$Se$_3$ crystal structure remains
intact away from the targeted areas is provided by Raman
spectroscopy. Figure 5 shows the Raman spectra taken on the
Bi$_2$Se$_3$ flake about 5 μm away from the Pd line (position 1), on
top of the Pd line (position 2), and on the Bi$_2$Se$_3$ flake directly
adjacent to the Pd line (positions 3 and 4). In the spectra
recorded at positions 1, 3, and 4, we observe phonon bands at
73, 132, and 176 cm$^{-1}$, which is typically found for Bi$_2$Se$_3$.
The widths of the lines are 5–8 cm$^{-1}$, which is also typical for
bulk Bi$_2$Se$_3$. These results confirm that the crystal structure of
the material is unchanged at these positions. We do not observe
the Raman bands on top of the Pd line (position 2) because the
Pd layer on the surface of the Bi$_2$Se$_3$ flake prevents the
propagation of the visible excitation light.

**CONCLUSIONS**

The combination of optical, TEM, EDS, and Raman spectroscopy with electrical measurements shows that Pd is absorbed by the Bi$_2$Se$_3$ crystal only in the targeted areas, allowing us to pattern superconductivity in Bi$_2$Se$_3$. More work is needed to determine the nature of superconductivity in Pd-doped Bi$_2$Se$_3$. Regardless of whether the patterned regions show topological superconductivity in their own right or just provide conventional superconductivity in proximity to topological insulator, the patterning provides a promising platform for building 2D topological devices.
B_i_3Se_3 nanocrystals of thickness between 70 and 100 nm were mechanically exfoliated onto 300 nm SiO_2 on Si substrates. Pd leads were patterned and deposited onto the nanocrystals using standard electron beam and optical lithography methods. The devices were annealed in a quartz tube furnace at a set temperature between 200 and 300 °C while flowing argon gas through the tube at a rate of 200 sccm. The set temperature was maintained for 1 h, after which the tube furnace was turned off and allowed to cool naturally. A second layer of palladium leads was added over the doped areas in order to ensure good contact for electrical measurements. Raman scattering spectra were measured in backscattering geometry using a Horiba Jobin-Yvon T64000 spectrometer equipped with an Olympus microscope. The 514.5 nm line of the Ar+ laser was used for excitation. The laser power was kept below 1 mW to avoid overheating of the sample. The size of the laser probe was about 2 μm in diameter. The spectra were recorded with 2.5 cm⁻¹ spectral resolution.

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