Josephson Coupling Realized in Graphite-Based Vertical Junction

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We confirmed the Josephson effect in vertically proximity-coupled junctions prepared by sandwiching a 43-nm-thick exfoliated graphite layer between two superconducting electrodes. Josephson coupling with well-controlled contact characteristics was established by thermal deposition of electrodes on both sides of freshly cleaved graphite surfaces. The genuine Josephson coupling through the c-axis graphite was confirmed by the critical current modulation in in-plane magnetic fields (Fraunhofer pattern) and the response to the microwave irradiation (Shapiro steps). This scheme can be potentially utilized to fabricate atomically thin vertically coupled nanodevices based on assorted cleavable layered materials.

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Electron-beam lithography was used to pattern electrodes in bulk 11) and exfoliated graphite. 12) The fabrication processes are illustrated in Fig. 1. A bottom electrode was directly evaporated on freshly cleaved graphite. Then, by using a stack of sacrificial layers, the entire structure was flipped over and attached to a new substrate. The top electrode was then evaporated on the other side of the graphite surface, which was also cleaved to obtain a clean surface with minimal mechanical or chemical damage. Details of the processes are as follows. First, a water-soluble poly(4-styrenesulfonic acid) (PSS) layer was spin-coated on a sacrificial substrate, followed by spin coating of a 1.2-μm-thick LOR resist (MicroChem) layer. The LOR resist layer would be used as a mechanical support during the device fabrication by utilizing its chemical stability against various solvents. 14) We then used a piece of Scotch-brand tape to exfoliate a thin graphene layer from crystalline natural graphite 1) on a sacrificial substrate covered with PSS and LOR layers [Fig. 1(a)]. At this stage, the thickness of the graphite layer was determined. In this report, we focus on a 43-nm-thick graphite sample. Since few-layer graphene and even monolayer graphene can be distinguished under an optical microscope, this method is readily applicable to any atomically thin graphene flakes.

Electron-beam lithography was used to pattern electrodes with a 950 K poly(methyl methacrylate) (PMMA) layer. Following the electron-beam exposure, the PMMA layer was
developed and rinsed with methyl isobutyl ketone (MIBK) developer and isopropyl alcohol (IPA), respectively. In this process, the LOR and PSS layers underneath the PMMA layer did not react with MIBK and IPA and remained stable. We deposited a stack of layers of Ti/Al/Au (5 nm/50 nm/5 nm thick) in series. Ti was used as an adhesion layer. The Au capping layer was deposited to protect the Al layer from oxidation in the ambient environment and in the rest of the processes. The lift-off was done in a hot bath of xylene, which selectively dissolved PMMA but did not react with LOR or PSS [Fig. 1(b)]. As shown in Fig. 1(c), we set the entire substrate afloat on water to dissolve the water-soluble PSS layer and detach the sacrificial substrate. Then, the LOR layer floated on water while supporting the other fabricated structure. The entire structure was carefully recovered, flipped over, and attached to a new substrate [Fig. 1(d)]. The LOR layer was then eliminated in a hot LOR remover bath (MicroChem RemoverPG) and rinsed with IPA and hexane [Fig. 1(e)]. As shown in Fig. 1(f), the device fabrication was completed by depositing the top electrode consisting of a stack of Ti/Al/Au (5 nm/200 nm/5 nm thick) layers by the electron-beam evaporation and lift-off in an acetone bath.

Figures 2(a) and 2(b) show optical images of a sample taken at the fabrication steps of Figs. 1(b) and 1(e) (before and after the flip-transfer process), respectively. Figure 2(c) shows the same device after completing the entire processes. Four junctions were fabricated on a substrate in a batch.

Figure 3(a) shows the temperature dependence of resistivity \( \rho_c \) of JJ1 above the superconducting transition temperature of aluminum. A broad resistivity maximum of around 50 K is a feature routinely observed in thin graphite samples,\(^ {12,15,16} \) which has been explained by the competition between the carrier density and mobility of opposite temperature dependences. Temperature dependence as well as the order of magnitude of the resistivity of JJ1 measured in a two-terminal configuration indicates that the contact resistance in our device did not overwhelm the intrinsic transport properties of graphite along the c-axis. Figure 3(b) shows the current–voltage \( (I-V) \) characteristics of JJ1 at \( T = 70 \) mK. One sees a clear Josephson current as large as \( I_c = 0.8 \mu \text{A} \) and a normal-state junction resistance of \( R_N = 4.0 \Omega \) above \( I_c \). In the current sample geometry, \( R_N \) may have been underestimated as the normal-state junction current above \( I_c \) was not confined within the junction area. The other two Josephson junctions in Fig. 2(c) showed behaviors qualitatively similar (not shown) to those of JJ1.

Figures 2(a) and 2(b) show optical microscopy images of the devices (a) after the first lift-off process in Fig. 1(b), (b) after removing LOR on the transferred structure in Fig. 1(e), and (c) in the final step in Fig. 1(f). The widths of the top and bottom electrodes are 2.8 and 2.5 \( \mu \text{m} \), respectively.

Fig. 1. Device fabrication processes of a vertical graphite Josephson junction. (a) Exfoliation of graphite on an LOR resist layer. (b) A metallic bottom electrode is deposited using an electron-gun evaporator. (c) By floating the substrate on water, the PSS layer is dissolved, followed by detaching the sacrificial substrate from the LOR layer. (d) The floating LOR layer, which supports the remaining graphite layer and base electrodes, is flipped over and attached to a new substrate. (e) The LOR layer is removed. (f) A metallic top electrode is deposited.

Fig. 2. Optical microscopy images of the devices (a) after the first lift-off process in Fig. 1(b), (b) after removing LOR on the transferred structure in Fig. 1(e), and (c) in the final step in Fig. 1(f). The widths of the top and bottom electrodes are 2.8 and 2.5 \( \mu \text{m} \), respectively.

Fig. 3. (a) Temperature dependence of resistivity \( \rho_c \) of JJ1. (b) \( I-V \) characteristics of JJ1, featuring Josephson supercurrent of \( I_c = 0.8 \mu \text{A} \). The supercurrent branch is slightly tilted due to the voltage drift of preamplifier during the measurement, which appears at random for different bias current sweeps.
In in-plane magnetic fields aligned along the length direction of the bottom electrode, the supercurrent is periodically modulated [Fig. 4(a)], exhibiting a Fraunhofer-like diffraction pattern. The periodicity \( H_0 = \Phi_0 / (W(d_i + 2L_0)) \) should be the magnetic field corresponding to a flux quantum \( \Phi_0 = h/2e \) threading the junction area \( A = W(d_i + 2L_0) \), for the width of the bottom electrode \( W = 2.5 \mu m \), the thickness of graphite \( d_i = 43 \text{ nm} \), and the London penetration depth of superconducting electrodes \( L_0 \). Here, the thickness of graphite was determined by atomic force microscopy after completing all the measurements. The observed \( I_c \) modulation in Fig. 4(a) shows a good fit to the expression \( I_c(H) = I_c(0) \sin(\pi H / H_0) / (\pi H / H_0) \) with the best-fit value of \( L_0 = 73 \text{ nm} \). This provides a clear confirmation that the supercurrent arose from the Josephson coupling through the \( c \)-axis graphite rather than any artifacts such as microshorting across the graphite. Another conclusive evidence of genuine Josephson coupling is the response of the junction to the microwave irradiation. For the microwave frequency \( f_{\text{mw}} \), the ac Josephson effect leads to quantized voltage steps (i.e., Shapiro steps) at the bias voltage of \( V = nhf_{\text{mw}} / 2e \) \( (n \) is an integer, \( h \) the Planck constant, and \( e \) the electron charge). As shown in Fig. 4(b), voltage steps have 11.1 \( \mu V \) intervals for \( f_{\text{mw}} = 5 \text{ GHz} \), which is close to the theoretical expectation of 10.3 \( \mu V \). The inset in Fig. 4(b) shows the overall variation of the Shapiro-step height \( \Delta V \) (height of the black region) with varying microwave amplitude \( P_{\text{mw}}^{1/2} \). It reveals a Bessel-function-like \( P_{\text{mw}}^{1/2} \) dependence of \( \Delta V \). Each Shapiro-step region is more elongated than that in an underdamped Josephson junction because of the enhanced damping by the normal-conductive graphite shunting layer.\(^{17}\)

Various promising extension of this fabrication technique is conceivable. First, this scheme is applicable to any cleavable materials (graphite in this report), including insulating MoS\(_2\) or h-BN, which provides atomically thin crystalline tunneling barriers, desirably replacing the amorphous metal oxides. Second, the thickness of the cleavable materials can be arbitrarily scaled down to a mono-atomic layer. Combining these materials with superconductors enables one to study the transport in extremely short ballistic Josephson junctions, which were theoretically predicted long time ago\(^{18}\) but have not been realized to date. Third, using this approach, one can directly evaporate assorted metal electrodes on the cleaved layers by minimizing oxidation or degradation of the interface at the contacts. With evaporation of ferromagnetic electrodes, this scheme can be utilized to fabricate a perfect spin filter with few-layer graphene or magnetic tunnel junctions based on an atomically thin crystalline insulating layer with minimal spin-flip scatterings at the contacts as well as in the insulating layer itself.

In summary, we have developed a fabrication scheme for vertical devices out of cleavable layered materials with highly transparent metal contacts. To demonstrate the usefulness of this scheme, we thermally deposited superconducting electrodes on both surfaces of cleaved natural graphite layers. In these vertically proximity-coupled graphite junctions, we confirmed the genuine Josephson coupling. Our fabrication scheme is applicable to realizing \( c \)-axis nanodevices based on any cleavable materials with the double-sided metallic electrodes of well-controlled junction characteristics.

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