Scanning tunneling spectroscopy of proximity superconductivity in epitaxial multilayer graphene

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(Rceived 9 October 2015; published 7 January 2016)

We report on spatial measurements of the superconducting proximity effect in epitaxial graphene induced by a graphene-superconductor interface. Superconducting aluminum films were grown on epitaxial multilayer graphene on SiC. The aluminum films were discontinuous, with networks of trenches in the film morphology reaching down to exposed graphene terraces. Scanning tunneling spectra measured on the graphene terraces show a clear decay of the superconducting energy gap with increasing separation from the graphene-aluminum edges. The spectra were well described by BCS theory. The decay length for the superconducting energy gap in graphene was determined to be greater than 400 nm. Deviations in the exponentially decaying energy gap were also observed on a much smaller length scale of tens of nanometers.

Each movie frame is 10 mK in temperature of 10 mK for measurements [15]. Tunneling spectroscopy was performed by measuring the tunneling differential conductance, \( dI/dV \), using a lock-in detection scheme with modulation frequency of 141 Hz and a root-mean-square modulation amplitude of 15 \( \mu \)V added to the sample bias. The effective electron temperature was extracted from tunneling spectra on superconducting aluminum. Electrochemically polished Ir tips were used for tunneling probes. Few-layer graphene films were grown on a (Si-face) SiC substrate by high temperature thermal sublimation of Si [16]. The aluminum films were grown on the graphene substrate by molecular beam epitaxy at a rate of 0.04 nm/s, with the substrate temperature initially held at 20 °C for the first 4.5 nm of growth, followed by 350 °C for the rest of the film growth for a total thickness of \( \approx 200 \) nm. The films were then transferred in ultrahigh vacuum (UHV) and loaded into the STM module, and cooled to our base temperature of 10 mK for measurements [15]. The aluminum grew in atomically smooth films with very uniform height, but with deep voids exposing the bare graphene terraces, as shown in the atomic force microscopy (AFM) image in Fig. 1(a). The AFM measurements were done at room temperature after the sample was removed from the STM system.

The experiments were carried out in a custom-built ultralow-temperature scanning tunneling microscopy (STM) system operating at 10 mK [15]. Tunneling spectroscopy was performed by measuring the tunneling differential conductance, \( dI/dV \), using a lock-in detection scheme with modulation frequency of 141 Hz and a root-mean-square modulation amplitude of 15 \( \mu \)V added to the sample bias. The effective electron temperature was extracted from tunneling spectra on superconducting aluminum. Electrochemically polished Ir tips were used for tunneling probes. Few-layer graphene films were grown on a (Si-face) SiC substrate by high temperature thermal sublimation of Si [16]. The aluminum films were grown on the graphene substrate by molecular beam epitaxy at a rate of 0.04 nm/s, with the substrate temperature initially held at 20 °C for the first 4.5 nm of growth, followed by 350 °C for the rest of the film growth for a total thickness of \( \approx 200 \) nm. The films were then transferred in ultrahigh vacuum (UHV) and loaded into the STM module, and cooled to our base temperature of 10 mK for measurements [15]. The aluminum grew in atomically smooth films with very uniform height, but with deep voids exposing the bare graphene terraces, as shown in the atomic force microscopy (AFM) image in Fig. 1(a). The AFM measurements were done at room temperature after the sample was removed from the STM system.

The areas of exposed graphene substrate within the aluminum voids are of submicron length scale [see Figs. 1(a) and 1(b)]. Inspection of the terraces between the aluminum film edges shows pristine graphene surfaces, as observed in Fig. 1(c). Multiple graphene layers are evident, first from the
atomic step indicated in Fig. 1(b), and second from the moiré pattern observed in Fig. 1(c). The latter is due to a rotational misalignment between the top two layers of graphene with an angle of $\approx 5^\circ$. Such a rotation is commonly encountered in epitaxial graphene on SiC and effectively decouples the top graphene layer, yielding single-layer-like electronic properties [17,18]. The disorder potential seen by the carrier in this decoupled graphene layer is very low, as determined in our previous STM experiments [17,18].

We now focus on proximity-induced superconductivity of the region measured along the dashed line indicated in Fig. 1(b). Figure 2 displays the tunneling spectra starting at the aluminum edge on the right side of the graphene terrace in Fig. 1(b), which corresponds to $x = 0$. To determine the energy gaps we fit the spectra to the Maki theory, which is an extension of the BCS theory, accounting for effects of orbital depairing, the Zeeman splitting of the spin states, and spin-orbit scattering [19,20]. The fitting parameters for zero field are the energy gap $\Delta$, the orbital depairing parameter $\zeta$, and the effective electron temperature $T_{\text{eff}}$. The aluminum spectrum at $x = 0$ is well fit by the modified BCS theory with a superconducting gap of $(180.5 \pm 0.3) \mu\text{eV}$ [21]. This value is in good agreement with previous measurements of aluminum films [22]. Similarly, when we measure tunneling spectra on the exposed graphene terrace, we likewise observe well-defined superconducting tunneling spectra in graphene that again obey the modified BCS theory. At a distance of 41 nm from the aluminum edge, the superconducting gap is on the order of 100 $\mu$eV and decreases with growing distance from the aluminum edge. A normal state spectrum is, however, never observed in the present case, since the area of the graphene terrace is too small for proximity effects to fully decay from all the surrounding aluminum edges.

Figure 3(a) shows the location-dependent tunneling spectra in a 2D color graph along the dashed white line in Fig. 1(b). The superconducting gap (brown-yellow color) is observed throughout the spatial range along with well-defined coherence peaks (dark green) outside the gap. Each spectrum in Fig. 3(a) is fit to the modified BCS theory and the resulting superconducting gap is plotted in Fig. 3(b). An abrupt drop in the gap energy is observed next to the graphene-aluminum interface. Although such a sudden change in gap energy can be expected from theory and is observed in spatial measurements [4], we cannot rule out the effect of the finite probe tip radius sampling the several-dozen–nanometer-high sidewall of the aluminum film edge as we approach it, giving an abrupt change in gap energy before the tip samples the graphene terrace at the bottom of the graphene-aluminum interface. Following the abrupt drop, the gap size decays and reaches a minimum at around $x = 325$ nm, and then increases again.

FIG. 1. Growth of superconducting aluminum films on epitaxial graphene on a SiC substrate. (a) Large AFM scan of the aluminum topography showing pits between the aluminum terraces which reach down to the top graphene layer. The height scale covers a range of 198 nm from dark to bright. (b) STM image of a trench region between aluminum islands. The white arrows indicate a monolayer graphene step, and the dashed line traces the position of the spectroscopy measurements in Figs. 2 and 3. (c) High-resolution STM image of the graphene lattice obtained at the location marked by the red square in (b). The larger wavelength modulations are due to a moiré pattern with period of $\approx 2.8$ nm due to rotational misalignment of $\approx 5^\circ$ between the top and second graphene layers.

FIG. 2. Graphene superconducting tunneling spectroscopy. Differential tunneling spectra (symbols) measured at several lateral positions from an aluminum-graphene edge at $\Delta x = 0$ (see Fig. 3). The solid lines are nonlinear fits using the modified BCS theory by Maki [19,20], with gap energies indicated on the right of the graph [21]. The effective temperature of $T_{\text{eff}} = 232$ mK, representing the residual electrical noise in the system, was determined from the best fit to the aluminum spectrum at $x = 0$ and subsequently held fixed to extract the distance-dependent gap width on graphene. The error in the gap energy was determined from the chi-square minimization in nonlinear least-square fits to the Maki theory.
yielding a graphene coherence length of $\xi = (429 \pm 9)$ nm [21].

Interestingly, deviations of 10% – 20% from a simple monotonic decay are observed upon a closer examination of the distance-dependent gap values in Fig. 3(b). Possible explanations for these fluctuations include oscillations in the order parameter due the formation of a graphene electron resonator with the graphene terraces surrounded by aluminum islands. Oscillations in the supercurrent density have been observed in transport measurements in fabricated graphene resonators coupled to superconducting leads [9,10]. A second possibility may be due to the role of disorder in the graphene lattice. Recent spatial STM measurements of single atomic layers of Pb on silicon have shown that disorder in the 2D limit can significantly affect the superconducting order parameter on a length scale much shorter than the coherence length [5]. Indeed, the graphene topography displayed in Fig. 3(c) shows small, $\approx$100-pm, vertical variations in the topography indicating some form of disorder. It appears as if some of the topographic changes were correlated with the energy gap oscillations [see vertical dashed lines connecting Figs. 3(b) and 3(c)], but the largest change in topography occurring at the graphene atomic step at $x \approx 100$ nm does not show a large variation in gap value, except for a few outlier points which resulted from poor data quality obtained right at the step edge. These topographic variations can also be seen in the STM image in the inset in Fig. 3(c), where the small variations appear as small-scale bulges in the graphene lattice. These features are possibly related to lattice strain. Strain in graphene is associated with pseudomagnetic fields [23–26]. It remains an interesting theoretical problem to determine whether/how pseudomagnetic fields would affect the graphene superconducting state.

In summary, we report spatial mapping of proximity-induced superconductivity in epitaxial graphene. Superconductivity was induced in graphene through aluminum films grown on epitaxial graphene on SiC substrates, which had exposed voids reaching down to the graphene terraces. The superconducting order parameter was determined to have a coherence length of $(429 \pm 9)$ nm [21]. The order parameter showed oscillations of $\approx$10% on a much smaller length scale of tens of nanometers. These oscillations may be due to the formation of an electron resonator [9,10] inside the voids in the aluminum film or due to disorder [5] in the graphene lattice. This Al-graphene system lays the groundwork for possible future scanning probe measurements on gated single-layer and bilayer graphene devices to investigate superconducting graphene in greater detail as a function of carrier density and Fermi wavelength.

F.D.N. greatly appreciates support from the Swiss National Science Foundation under Project No. 158468. J.H., D.Z., and W.C. acknowledge support under the Cooperative Research Agreement between the University of Maryland and the National Institute of Standards and Technology, Center for Nanoscale Science and Technology, Grant No. 70NANB10H193, through the University of Maryland. H.B. and Y.K. are partly supported by the National Research Foundation of Korea through Grant No. KRF-2010-00349. We would like to thank Steve Blankenship, Glen Holland, and Alan Band for technical assistance.
[21] All uncertainties reported represent one standard deviation.