Observation of gate-controlled superconducting proximity effect in microfabricated thin graphite films

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Abstract. We investigated the influence of the oxygen plasma etching on the electron transport in thin graphite films. The semimetallic temperature dependence of zero-bias resistance was observed for samples microfabricated with both Al mask and resist mask, but the possible damage by e-beam irradiation was observed in films with Al mask. In thin graphite films microfabricated by O$_2$ plasma with resist mask, the proximity-induced superconductivity was observed and the critical supercurrent and temperature strongly depend on the gate voltage.

1. Introduction
A thin graphite film with thickness less than $\sim 10$ nm, which was discovered in 2004 by Novoselov et al. [1], is a promising candidate for nanoelectronics materials due to its excellent electrical properties (strong electric field effect, high mobility) as well as the stability under ambient conditions, easy microfabrication by oxygen plasma etching, and low cost. Besides, it is regarded as a new material for research of mesoscopic physics since the carrier can be varied from hole to electron.

For both purposes, the microfabrication of the films is indispensable, but to our knowledge, systematic optimization of the microfabrication processes has not been done yet. Here, we focus on this point and investigate experimentally the effect of microfabrication processes on the electron transport of thin graphite films, and report the observation of superconducting proximity effect in microfabricated thin graphite films.

For the Cooper-pair transport in a single graphite layer (graphene), nonzero critical supercurrent through a superconductor(S)/graphene/S Josephson junction was theoretically predicted[3], and an ambipolar supercurrent with nonzero critical current at the Dirac point was confirmed experimentally in untreated graphene films.[4]
2. Results and discussion

2.1. Influence of oxygen plasma etching on transport

We used a grain of kish graphite as the starting material. We mechanically exfoliated the grain with adhesive tape and placed the produced thin films on a substrate.[1] As a substrate, we used highly doped Si wafer with a 300- nm layer of SiO$_2$ on the top. By using an optical microscope, we chose thin graphite films with thickness less than 10 nm. A 10 nm graphite film corresponds to 30 layers of graphene.

For the microfabrication by oxygen plasma etching, two kinds of masks are prepared for a single graphite film: aluminum mask (thickness: 50 nm) and resist mask (ZEP 520, positive resist). The fabrication process is as follows: First, an Al mask was placed on a thin graphite film by using standard e-beam lithography with positive resists, metal (Al) deposition, and lift-off. Then, a resist mask was placed close to the Al mask on the same film by using e-beam lithography, and the unmasked part of the film was removed with oxygen plasma (25 Pa, 50 W, 30 - 60 sec). After removing masks by acetone and potassium hydroxide (KOH), we connected Pd electrodes with thickness of 100 nm on the etched films. The scanning electron microscope image of a sample and its masks are shown in the main panel and the inset of Fig. 1(a), respectively.

Electron transport properties were measured by the four terminal method in a dilution refrigerator. Figure 2(a) shows the temperature dependence of zero-bias resistance for the graphite films masked by Al and by resist. In both cases, resistance saturates at low temperatures, corresponding to the semimetallic band structure. The band overlap is roughly estimated to be about 20 meV, which is consistent with the thickness ($\sim$ 10 nm) of the film.[1]

For comparison, in Fig. 2(b), we show results on an untreated film (Fig 2(b)) and a film which was treated with Ar ion bombardment (inset of Fig. 2(b)). Here, the Ar ion bombardment (1 keV, Ar pressure of $9 \times 10^{-4}$ Pa, 1 min) was carried out just before the metal deposition to improve the contact between the metal electrodes and the graphite film, and during it, the main part of the film was covered with e-beam resist. In untreated thin graphite films, the zero-bias resistance saturates at low temperatures, as is the case in the present measurements, while it shows the log $-T$ weak-localization type temperature dependence when the film is treated...
2.2. Superconducting proximity effect in microfabricated thin graphite films

In a S/thin graphite film/S structure, we have observed gate-controlled superconducting proximity effect and found some novel phenomena such as electron-hole symmetry breaking and reentrant behavior.[6, 7] The measurement of the junction width and length dependences of the supercurrent is needed for the further investigation of the phenomena. Thus, microfabrication of the thin graphite films is indispensable. Figure 1(b) shows a scanning electron micrograph of a sample with superconducting electrodes (Ti(3nm)/Al(100nm)/Ti(3nm)) with various separation from 0.3 to 0.6 \( \mu \)m. Here, a rectangular film was prepared using oxygen plasma etching with the resist mask.

Figure 3(a) shows the temperature dependence of the zero-bias resistance of a junction under a gate voltage of \( V_g = 75 \) V and 30 V. Below the superconducting transition of the electrodes (0.87 K), the resistance drops and vanishes at lower temperatures, depending on the gate voltage. Figure 3(b) is the current-voltage characteristics at 0.2 K for \( V_g = 75 \) and 30 V. Clear zero-voltage supercurrent is observed. Besides, it is obvious that the critical temperature and the critical supercurrent strongly depend on the gate voltage. The features are qualitatively the
Figure 3. (a) Temperature dependence of the zero-bias resistance of a S/thin graphite film/S junction shown in Fig. 1(b). The gate voltage was 75 V (○) and 30 V (●). (b) Current-voltage characteristics for the same sample. The gate voltage was 75 V (○) and 30 V (●).

The same as those obtained in untreated thin graphite films.[6]

3. Conclusion
We investigated the influence of the oxygen plasma etching on the electron transport in thin graphite films. Both under Al and resist masks the graphite film retained the semimetallic behavior, but the possible damage by e-beam irradiation was observed in films with Al mask. In microfabricated graphite films, the proximity-induced superconductivity was observed and the critical supercurrent and temperature strongly depend on the gate voltage.

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