Influence of microfabrication on superconducting properties of exfoliated thin films of layered superconductor NbSe$_2$: reactive ion etching

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Abstract. We have experimentally investigated the influence of the reactive ion etching (RIE) on the superconducting properties of exfoliated thin films of layered superconductor NbSe$_2$ through transport measurement. Wires with width of 2 $\mu$m and 0.5 $\mu$m were fabricated from a single NbSe$_2$ film (thickness $\sim$ 65 nm) using RIE with CF$_4$ and O$_2$ gas mixture. While the 2-$\mu$m wires did not exhibit any distinguishable degradation in residual resistivity, residual resistance ratio, superconducting transition and current-voltage characteristics in the superconducting state, significant degradation was observed in the 0.5-$\mu$m wires.

1. Introduction
When the size of a superconductor approaches the characteristic length scales such as the coherence length and/or the magnetic penetration depth, the quantum confinement of Cooper pairs brings geometric effects. Thus, by controlling the geometry of the superconductor, one is able to manipulate mesoscopic superconducting states, which might lead to superconducting classical and quantum devices.

Mesoscopic superconducting effect manifests itself in vortex states.[1] In a mesoscopic type-II superconductor with several quantum vortices, the arrangement of the vortices depends not only on the vortex-vortex interaction but also on the interaction between a vortex and the sample edge, so that the triangular Abrikosov vortex lattice, which is characteristic of bulk superconductors, is deformed into a multivortex state (MVS) in which the vortex arrangement is strongly influenced by the sample shape, or a giant vortex state (GVS) in which the multiple vortices coalesce.[2, 3, 4, 5]

The common method of obtaining a shape-defined mesoscopic superconductor is the electron beam lithography followed by the deposition of superconducting materials in vacuum. So far, we have used electron-beam-evaporated aluminum as a material of mesoscopic superconductors to experimentally investigate the vortex states in mesoscopic superconductors. By using our original small tunnel junction method,[6, 7] we successfully confirmed the existence of a giant vortex and transitions between different MVSs or between an MVS and a GVS in mesoscopic circular and square thin films. These transitions were induced by an applied magnetic field [8, 9] as well as by a locally injected supercurrent.[10, 11, 12, 13] However, the controllability of the mesoscopic superconducting states was limited by the existence of defects which pin the
vortices. Actually in our aluminum samples, while the lateral dimensions are well controlled by the state-of-the-art electron beam lithography system, the control of the vertical dimension is poor because of the surface roughness, which is inevitable in evaporated aluminum films.

For this reason, we are looking for an alternative material for the study of mesoscopic superconductivity, and focusing on exfoliated thin films of layered superconductors.

Recently, the mechanical exfoliation technique, called the Scotch tape method, developed in the graphene research[14, 15], has been applied to layered superconductors, and thin superconductors with atomically flat surface can be easily obtained.[16, 17, 18] Such atomically flat superconductors are able to resolve the above defect problem. For the application of the exfoliated thin superconductors to the mesoscopic superconductivity research, one need to shape the lateral dimensions. In the graphene research, the reactive ion etching (RIE) is commonly used to shape the sample. The extremely high mobility is maintained even after the RIE process.[19] Here, we apply the RIE to the thin films of layered superconductors, and investigate the influence of the RIE on the superconducting properties.

2. Experiment

As a layered superconductor, we used NbSe$_2$. Optical microscope images of the samples are shown in Fig. 1.

For the fabrication of the RIE-treated sample (Fig. 1(a)), first an NbSe$_2$ flake with thickness of 65 nm was obtained using mechanical exfoliation of a bulk crystal on a SiO$_2$/Si substrate. Then RIE was performed with resist mask of ZEP-520a (Zeon Co.), gas mixture of CF$_4$:O$_2 = 24$ Pa:$2.7$ Pa, a power of 50 W, and for 1 min to form wires with widths of 2 $\mu$m and 0.5 $\mu$m from a single flake. Finally, Au/Cr electrodes are connected to the flake. In this sample, electron transport of two wires with width of 2 $\mu$m (samples #2 and #3) and two wires with width of 0.5 $\mu$m wires (samples #4 and #5) with the same length (4 $\mu$m) were investigated. Also, as a reference, a sample of a pristine NbSe$_2$ flake (without RIE treatment) with thickness of 65 nm (sample #1) was prepared.

Electron transport of the samples were measured with four-terminal method in vacuum in a cryostat with appropriate cryogenic lowpass filters. The differential resistance was obtained by numerically differentiating the current-voltage characteristics.
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Figure 2. (a) Temperature dependence of zero-bias resistance of sample #5 (a RIE-treated wire with width of 0.5 µm) between 4 K and 300 K. (b,c,d) Temperature dependence of zero-bias resistance of samples #1 (no RIE treatment), #2 (a RIE-treated wire with width of 2 µm) and #5 around the superconducting transition. Residual resistivity (e), superconducting transition temperature ($T_C$) and the transition width (f), and the residual resistivity ratio (g) for all samples.

3. Results and discussion
All samples exhibited the superconducting transition around 7 K. Typical temperature dependence of zero-bias resistance between 4 K and 300 K is shown in Fig. 2(a). Also, the close-ups around the superconducting transition of samples #1 (no RIE treatment), #2 (a RIE-treated wire with width of 2 µm) and #5 (a RIE-treated wire with width of 0.5 µm) are shown in Figs. 2(b), (c) and (d), respectively. While the superconducting transition of wires with width of 2 µm (samples #2 and #3) was similar to that of a flake without RIE (sample #1), the transition of wires with width of 0.5 µm (samples #4 and #5) was relatively smeared.

To elucidate this point, we show the residual resistivity, superconducting transition temperature ($T_C$) and the transition width, and the residual resistivity ratio (RRR) for all samples in Figs. 2(e-g). Here, we define the transition width as the temperature range where the resistance are between the 5% and 95% of the normal state residual resistance, and $T_C$ as the midpoint of the transition width. Besides, the residual resistivity ratio is the ratio of the resistance at 300 K to the residual resistance at low temperatures. In Figs. 2(e) and (f),
Figure 3. (a, c, e) Current-voltage characteristics of samples #1(a), #3(b) and #4(c) for several temperatures. (b, d, f) Differential resistance plotted in the current-temperature plane for samples #1(b), #3(d) and #4(f), respectively. The biasing current was swept from negative to positive values.
while the resistivity, \( T_C \) and the transition width of samples \#1, \#2 and \#3 are almost the same, those of samples \#4 and \#5 exhibit clear difference from the others, indicating that the superconductivity of wires with width of 0.5 \( \mu \text{m} \) deteriorates, while that of wires with width of 2 \( \mu \text{m} \) does not. This conclusion is supported by the result of RRR. (Note that RRRs for samples \#2 and \#3 were not available due to missing resistance data at room temperature.)

Finally we discuss the current voltage characteristics. Figure 3 shows the current-voltage characteristics of samples \#1 (Figs. 3(a) and (b)), \#3 (Figs. 3(c) and (d)) and \#4 (Figs. 3(e) and (f)). The biasing current was swept from negative to positive values. In Figs. 3(b,d,f), the differential resistance is plotted in the current-temperature plane. The red regions around the zero current correspond to the zero-resistance state, and thus the upper edge of a red region corresponds to the critical current. The lines around the red regions in Figs. 3(b,d,f) correspond to steep voltage change in Figs. 3(a,c,e), which appear below the critical temperature \( \approx 7.2 \text{ K} \). These are presumably due to the phase slips. Both in Figs. 3(b) and (d), the boundaries of the red regions are clear, and several lines corresponding to phase slips are seen. In this way, Figs. 3(a) and (c) (3(b) and (d)) are similar to each other except for the current scale which is due to the difference in sample width, indicating again that the superconductivity of wires with width of 2 \( \mu \text{m} \) does not deteriorate due to the RIE. On the other hand, in Fig. 3(f), the boundary of the red region is blurred, and more lines corresponding to phase slips are seen in comparison with Figs. 3(b) and (d), indicating that there exist many phase slip centers. These results indicate that the wires with width of 0.5 \( \mu \text{m} \) are damaged by the RIE treatment.

4. Conclusions
We have experimentally investigated the influence of the reactive ion etching (RIE) on the superconducting properties of exfoliated thin films of layered superconductor NbSe\(_2\) through transport measurement. While the 2-\( \mu \text{m} \) wires did not exhibit any distinguishable degradation in residual resistivity, residual resistance ratio, superconducting transition and current-voltage characteristics in the superconducting state, significant degradation was observed in the 0.5-\( \mu \text{m} \) wires.

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