Influence of focused-ion-beam microfabrication on superconducting transition in exfoliated thin films of layered superconductor NbSe$_2$

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Abstract. We have experimentally studied the influence of the focused ion beam (FIB) microfabrication on the superconducting properties of exfoliated thin films of layered superconductor NbSe$_2$ through transport measurement. We observed significant decrease of the residual-resistance ratio (RRR), indicating the formation of defects by the FIB. Although clear superconducting transition was seen before the FIB microfabrication, after FIB it was blurred, and one sample exhibited insulating behavior. The possible origins of the changes in the superconducting properties are discussed.

1. Introduction

Atomic layers have attracted much attention in recent years. Rapidly developing technology of mechanical exfoliation of layered materials using sticky tapes and transfer/stacking of atomic layers, first developed in the graphene research[1, 2], have been widely used for various kinds of two-dimensional materials, which have various features such as metal, insulator, superconductor and so on.[3] Studies on thin film superconductors also benefit from these technological innovations.

Previously thin-film superconductors were mainly obtained by vacuum deposition and epitaxial growth, but in general deposited films include a lot of defects, and the substrate is limited for epitaxial layers. On the other hand, by utilizing the technology cultivated in graphene research, one is able to obtain superconducting thin films which are clean and atomically uniform. Accordingly, thin film superconductors have been studied more extensively[4, 5, 6] and also are expected as materials for next generation quantum devices. Here, note that for investigating detailed transport characteristics and making devices for applications, microfabrication is required.

There are several kinds of microfabrication techniques for layered materials. One is the reactive ion etching (RIE), which is commonly used for atomic layers such as graphene and hexagonal boron nitride. Extremely high mobility is kept in graphene even after the RIE microfabrication.[7] Another is the focused ion beam (FIB) milling, which is conventionally used for microfabrication of high-$T_C$ superconductors.[8, 9] According to the previous study, when bulk high-$T_C$ superconductors are microfabricated with FIB, damage is spread only over the range of several tens of nm from the surface.[10] On the other hand, the influence of FIB
microfabrication on thin layered superconductors has not been studied yet. Here, we investigate the influence of FIB microfabrication on the superconducting properties of niobium diselenide (NbSe$_2$), which is a layered superconductor with a bulk $T_C$ of $\sim$7.2 K.

2. Experimental

We obtained NbSe$_2$ flakes on a SiO$_2$/Si substrate by exfoliating a bulk crystal using Scotch tape[1, 2], but due to our poor technique, flakes consisted of several stacking layers, as seen in Fig. 1(a). Electrodes (Au (100 nm)/Cr (5 nm)) were connected to a flake using conventional electron beam lithography followed by metal deposition in vacuum. For the FIB milling, we used XVision 200DB (SII Nanotechnology Inc.) with the acceleration voltage of 30 kV and a dose of $\sim 2 \times 10^9$ gallium ions/µm$^2$.

We made three samples, #1, #2, and #3. Nominal thicknesses are 57 nm, 57 nm, 43 nm for samples #1, #2, and #3, respectively. Optical microscope images before and after the FIB microfabrication of sample #3 are shown in Figs. 1(a) and (b), respectively. The electron transport before and after the FIB microfabrication was investigated above $\sim 4.5$ K in vacuum in a cryostat with appropriate cryogenic lowpass filters. The zero-bias resistance was obtained by numerically differentiating the linear part of current-voltage characteristics around the origin with bias voltages typically less than 10 mV. Magnetic field was applied perpendicular to the substrate.

3. Results and discussion

Figure 2(a) shows the zero-bias resistance ($R$) as a function of the temperature before the FIB microfabrication. As shown in Fig. 2(b), the samples exhibited the superconducting transition with $T_C = 7.0$ K and the transition width $\Delta T_C \approx 0.1$ K. Here, we define $T_C$ as the temperature where the resistance becomes 50% of its value at 8 K ($R(8$ K)) and $\Delta T_C$ as the temperature width where the resistance drops from 90% to 10% of $R(8$ K). The residual-resistance ratio (RRR), defined as $R(270$ K)/$R(8$ K), is shown in Table 1. The FIB microfabrication induced striking change in the superconducting transition. Figure 2(c) shows the resistance variation in a wide temperature range after the FIB microfabrication. While the resistance of samples #1 and #2 slightly decreased with decreasing temperature ($dR/dT > 0$, metallic behavior), sample...
Figure 2.  (a) Zero-bias resistance is plotted as a function of the temperature for samples, #1, #2, and #3 before the FIB microfabrication. (b) Superconducting transition of sample #3.  (c) Zero-bias resistance is plotted as a function of the temperature for samples, #1, #2, and #3 after the FIB microfabrication.  (d-f) Resistance - temperature curves between 4.3 K and 7.6 K for samples #1(d), #2(e), #3(f) after the FIB microfabrication.

#3 exhibited an insulating behavior with $dR/dT < 0$. The residual-resistance ratio (RRR), defined as $R(270\text{ K})/R(8\text{ K})$ for samples with metallic behavior, is shown in Table 1. The RRR is dramatically deteriorated by the FIB microfabrication, indicating that the gallium ion beam introduced significant defects in the NbSe$_2$ flakes. The insulating behavior in sample #3 also
indicates damage due to the FIB treatment. These results present a great contrast to the above-mentioned previous work for high-$T_C$ superconductors.[10] The possible origins of the defects will be discussed below. Figs. 2(d-f) are the close-ups of the low-temperature resistance. By the FIB microfabrication, the superconducting transition to the zero-resistance state was washed out above 4.3 K for all samples. Although the sample width after the FIB microfabrication was the same for all samples, the low-temperature transport varied sample to sample. For sample #1, resistance slightly decreased below 6.9 K and exhibited a drop at 5.5 K. However the relative amount of the resistance drop was small, with the resistance ratio $R(4.3 \text{ K})/R(6.9 \text{ K}) = 0.96$. For sample #2, the resistance started to drop at 7.0 K, and it took 50% of $R(7 \text{ K})$ at 4.7 K. The resistance ratio $R(4.3 \text{ K})/R(7.0 \text{ K}) = 0.12$. For sample #3, while it displayed an insulating behavior, small resistance drop still appeared between 5.0 K and 5.8 K.

| Sample | Before RIE behavior | Residual-resistance ratio (RRR) | After RIE behavior | Residual-resistance ratio (RRR) |
|--------|---------------------|-------------------------------|-------------------|-------------------------------|
| #1     | metallic            | 21.8                          | metallic          | 1.15                          |
| #2     | metallic            | 17.6                          | metallic          | 2.48                          |
| #3     | metallic            | 18.0                          | insulating        |                               |

To confirm whether the resistance drops seen in all samples after the FIB microfabrication originate from superconductivity, we investigated the magnetic field dependence of the resistance. The results are shown in Fig. 3. Figures 3(a,c,e,g) are resistance of sample #3 before the FIB microfabrication, resistances of samples #1, #2, and #3 after the FIB microfabrication, respectively, plotted in the magnetic field ($B$)-temperature ($T$) plane. The resistance range of the color map is approximately between the minimum and maximum values of the resistance for each plot. Figures 3(b,d,f,h) are resistance of sample #3 before the FIB microfabrication, resistances of samples #1, #2, and #3 after the FIB microfabrication, respectively, plotted as a function of temperature for several magnetic fields. In Fig. 3(a), for sample #3 before FIB microfabrication, the boundary between the blue and red regions, indicated by dashed lines, corresponds to the critical magnetic field. The critical magnetic field increases linearly with decreasing temperature. The other samples (samples #1 and #2 before the FIB microfabrication) exhibited the same characteristics (not shown). For samples after the FIB microfabrication, in Figs. 3(c,e,g), the boundary between the blue and red regions, corresponding to a characteristic magnetic field for the resistance change, shows a trend similar to the one in Fig. 3(a), as indicated by dashed lines. That is, the characteristic magnetic field linearly increases with decreasing temperature. (Note that in Fig. 3(g), this is seen only at $T < 5.5 \text{ K}$.) Also, in Fig. 3(b) before the FIB treatment, the resistance drop becomes less steep as the magnetic field increases. This trend is also seen in Figs. 3(d) and (f). Thus, we conclude that the resistance drop seen in samples after the FIB microfabrication is related to the superconductivity.

Finally, we discuss the origin of the change in the superconducting properties due to the FIB microfabrication. Here, we point out three possibilities. The first is related to the disorder. As clearly seen in RRR values in Table 1, the FIB induces many defects. Defects, or disorder, can cause broadening of the superconducting transition, and in the limit of the strong disorder, the superconductor-insulator transition, which was intensively studied theoretically and experimentally as a dissipation-driven quantum phase transition.[11, 12] The decrease of
Figure 3. (a,c,e,g) Magnetic field and temperature dependence of resistance of sample #3 before the FIB microfabrication, resistances of samples #1, #2, and #3 after the FIB microfabrication are plotted, respectively. Dashed lines indicate boundaries between blue and red regions. (b,d,f,h) The resistances for several magnetic field values are plotted as a function of temperature for sample #3 before the FIB microfabrication, samples #1, #2, and #3 after the FIB microfabrication, respectively.
the superconducting transition temperature is explained as a precursor of the superconductor-insulator transition. The second possible origin is the intercalation of the gallium atoms in NbSe$_2$ crystals. It is known that the gallium-intercalated NbSe$_2$ exhibits lower $T_C$ as compared to the pristine NbSe$_2$, depending on the amount of gallium.[13] For example, $T_C$ of Ga$_{0.1}$NbSe$_2$ is 2.7 K. The FIB might prompt the non-uniform intercalation of gallium atoms, leading to spatially non-uniform superconducting transition. The third is the cleavage of NbSe$_2$ layers by the FIB. The impact of the gallium ions might widen the interlayer spacing of NbSe$_2$, forming effective monolayer and/or few layer NbSe$_2$, which are still electrically connected to each other. It is known that $T_C$ decreases as the layer number of NbSe$_2$ decreases, and $T_C \approx 2 – 3$ K for monolayer NbSe$_2$.[4, 5, 6]

The detailed origin of the change in the superconducting properties due to the FIB microfabrication is not clear at this moment. Further experimental and theoretical researches are needed for the full understanding of the microfabrication of the layered materials.

4. Conclusions
We have experimentally studied the influence of the focused ion beam (FIB) microfabrication on the superconducting properties of exfoliated thin films of layered superconductor NbSe$_2$ through transport measurement. The sample is an FIB processed wires with width of 2 $\mu$m. We observed significant decrease of RRR and the deterioration of the superconducting properties. The origin of these effect is discussed.

Acknowledgments
This work was supported by JSPS KAKENHI Grant Number JP15H05867 [Hybrid Quantum Systems] and University of Tsukuba Basic Research Support Program Type B. The FIB microfabrication was conducted at the AIST Nano-Processing Facility, supported by “Nanotechnology Platform Program” of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

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