$T_c$ depression and superconductor-insulator transition in molybdenum nitride thin films

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Abstract. We have studied the $T_c$ depression and the superconductor-insulator transition (SIT) in molybdenum nitride (MoN) thin films. Thin films were fabricated by reactive DC magnetron sputtering method onto (100) MgO substrates in the mixture of Ar and N$_2$ gases. Several dozen MoN thin films were prepared in the range of 3 nm < thickness $d$ < 60 nm. The resistance was measured by a DC four-probe technique. It is found that $T_c$ decreases from 6.6 K for thick films with increase of the normal state sheet resistance $R_{sq}$ and experimental data were fitted to the Finkel’stein formula using the bulk superconducting transition temperature $T_{c0} = 6.45$ K and the elastic scattering time of electron $\tau = 1.6 \times 10^{-16}$ s. From this analysis the critical sheet resistance $R_c$ is found about 2 kΩ, which is smaller than the quantum sheet resistance $R_Q$. This value of $R_c$ is almost the same as those for 2D NbN films. The value of $\tau$ for MoN films is also the similar value for NbN films $1.0 \times 10^{-16}$ s, while $T_{c0}$ is different from that for NbN films 14.85 K. It is indicated that the mechanism of SIT for MoN films is similar to that of NbN films, while the mean free path $\ell$ for MoN films is larger than that for NbN films.

1. Introduction
To study low-dimensional superconducting devices like superconducting single-photon detectors [1, 2] and superconducting transition edge detector [3, 4], it is necessary to investigate the effects of disorder in low-dimensional superconductors on the superconductor-insulator transition (SIT). There are mainly two scenario to understand the SIT mechanism. One is the dirty boson scenario. According to this scenario the Cooper pairs exist even in the insulator side. They are localized at a sheet resistance close to the quantum sheet resistance $R_Q (= \hbar/4e^2 \approx 6.45$ kΩ) as observed in Bi [5, 6], Pb [5] and InO [7]. The other is the fermionic scenario. This scenario is based on the idea that the disorder-enhanced Coulomb repulsion prevents Cooper pairing. Both the energy gap $\Delta$ and $T_c$ decrease with the same rate to zero at SIT as the disorder, for instance, the sheet resistance $R_{sq}$ increases. Finkel’stein [8] shows that the $T_c$ depression is determined from the values of bulk $T_{c0}$ and elastic scattering time $\tau$. This indicates that the $R_c$ at the SIT is not universal but depends on the material. $T_c$ depression of NbN [9, 10] and MoGe [11] induced by disorder has been explained by this scenario.
The thin film with lower $T_c$ is preferable for low-dimensional superconducting devices because the material with a smaller superconducting gap can show a higher sensitive response. However, the thin film with high resistivity $\rho$ have a disadvantage of slow response speeds because of the large kinetic inductance. Therefore it is necessary to search materials with lower $T_c$ and $\rho$ for the sensitive superconducting detectors. Molybdenum nitride (MoN) has attracted attentions because of the possibility for a new device-material to satisfy these demands. In this paper, we report the $T_c$ depression and the SIT in MoN thin films. The results of the suppression of $T_c$ are analyzed by the Finkel’stein formula from localization theory [8]. The parameters obtained by the analyze are compared with those for NbN films.

2. Experimental detail

MoN films were deposited on (100) MgO substrates by reactive DC magnetron sputtering method. Namely Mo was sputtered in the presence of a mixture of Ar and $N_2$ gases while keeping the total gas pressure at 0.27 Pa [12]. The gas ratio of $N_2$, $p(N_2)$, was controlled by the fixed flow rates of Ar $f(\text{Ar})$ and $N_2$ $f(N_2)$ gases. The gas ratio $p(N_2)$ is defined as $p(N_2) = f(N_2) / (f(\text{Ar}) + f(N_2))$. Table 1 shows the $p(N_2)$ dependences of chemical composition, resistivity at 300 K $\rho(300\text{K})$ and $T_c$ in thin films [13]. The chemical composition in thin films was measured by wavelength dispersive X-ray spectroscopy (WDS). $N_2$ composition and $\rho(300 \text{ K})$ monotonically increase as increasing $p(N_2)$. However, $T_c$ takes the maximum value at $p(N_2) = 9.1\%$. In this report we fabricated MoN films keeping the optimum value of $p(N_2) = 9.1\%$. The crystal structures of films were investigated by X-ray diffraction analysis. The films have clear (200) and (400) peaks with the lattice constant $d_0 = 0.4168 \text{ nm}$. According to the previous research [14] for lattice constant $d_0$ and $T_c$, it was reported that MoN has $d_0 = 0.4213 \text{ nm}$ and $T_c \sim 12 \text{ K}$ and $\gamma$-Mo$_2$N cubic has $d_0 = 0.4163 \text{ nm}$ and $T_c \sim 5 \text{ K}$. Therefore, we suppose that present films take $\gamma$-Mo$_2$N cubic structure.

| flow rate (SCCM) $f(\text{Ar})$ | Gas Ratio $f(N_2)$ | $p(N_2)$ (%) | $N_2$ composition (%) | $\rho(300 \text{ K})$ (\(\mu\text{\Omega m}\)) | $T_c$ (K) |
|-----------------|-----------------|----------------|-------------------|------------------|---------|
| 50              | 0               | 0              | 0                 | 0.045            | 0.96    |
| 50              | 5               | 9.1            | 23                | 1.3              | 6.60    |
| 50              | 10              | 17             | 27                | 1.4              | 6.56    |
| 50              | 21.7            | 30             | 35                | 2.0              | 5.16    |
| 50              | 30              | 38             | 40                | 2.6              | 3.56    |

Table 1. $N_2$ concentration, $\rho(300 \text{ K})$ and $T_c$ as a function of the gas ratio for thick films.

Various films with different thicknesses $d$ were prepared by changing the sputtering time because of the linear relation between the thickness and the sputtering time. Several dozen films were fabricated in the range of $3 < d < 60 \text{ nm}$. The films were patterned in a thin strip using a photolithography and etching procedure, where the width $w$ and the length $l$ between the voltage terminals of the strip were 0.15 mm and 2 mm, respectively. The resistance $R$ was measured by a standard dc four-probe technique in a temperature range $2 \leq T \leq 300 \text{ K}$. The sheet resistance $R_{sq}$ is calculated through the equation $R_{sq} = Rw/l$.

The sample pattern is also suitable for measuring the Hall voltage. We applied a magnetic field of up to $\pm 5 \text{ T}$ perpendicular to the film surface in order to obtain the carrier density from the Hall coefficient $R_H$ based on the free electron model $R_H = -1/ne$. 

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Figure 1. (a) $T$ dependence of $R_{sq}$ in MoN thin films. (b) $R_{sq}^N$ dependence of $T_c$ for MoN thin films. The solid line is calculated from Eq. (1), using $T_{c0}$ and $\tau$ as fitting parameters. Each figure corresponds to the specimen number.

3. Results and discussion

Figure 1(a) shows $R_{sq}-T$ curves for MoN films with various thicknesses [13]. Even for thin films with $d < 10$ nm (No. 9 ~ 12), the $R_{sq}-T$ shows a sharp superconducting transition without quasi-reentrant behavior. This behavior indicates that all superconducting films are homogeneous. The determination of the critical sheet resistance $R_c$ from Fig. 1(a) is difficult because of the limitation of measurement temperature to over 2 K. However, the $R_c$ can be estimated from the expression for $T_c(R_{sq})$ derived by Finkel’stein in the following paragraph.

Figure 1(b) shows $R_{sq}^N-T_c$ curves. Here, the normal sheet resistance $R_{sq}^N$ is estimated by following procedures. The values of $R_{sq}^N$ for several films were obtained from the extrapolation of $1/R_{sq}(H)$ versus $1/H$ to $1/H = 0$. It is found that the empirical power law relation $R_{sq}^N = 0.967R_{sq}(10K)^{1.01}$ is hold. $R_{sq}^N$ for all films in Fig. 1(b) were determined from $R_{sq}(10K)$ [13]. We can fit the theoretical model to experimental data in Fig. 1(b) to confirm the fermionic scenario and estimate the $R_c$ of the present MoN series. In the early stage of the investigation for the effect of disorder on $T_c$, Maekawa and Fukuyama proposed a theory for the suppression of $T_c$ due to enhanced Coulomb interactions in the presence of localization effects in a 2D disordered system [15]. Furthermore, Finkel’stein obtained the following expression from the renormalization group equation [8]

$$T_c = T_{c0} \exp(-1/\gamma) \left\{ \frac{1 + \sqrt{r/2}}{\gamma - r/4} \right\}^{1/\sqrt{2r}},$$

where $T_{c0}$ is the bulk superconducting transition temperature, $\gamma = 1/\ln(k_B T_{c0} \tau/h)$, $r = R_{sq}^N/(2\pi^2 \hbar/e^2)$ and $\tau$ is the elastic scattering time of electron. The solid line is calculated from Eq. (1) using the two values $T_{c0} = 6.45$ K and $\tau = 1.6 \times 10^{-16}$ s ($\gamma = 0.1128$) as fitting parameters. Although the $T_c$ data is restricted to the films with $T_c > 2$ K due to the measurement range of $T$, the value of $R_c$ can be estimated to be nearly $\sim 2$ kΩ from the well extrapolation of Eq. (1) for $T_c(R_{sq})$ to zero.
In order to compare the $R_{sq}^N$ dependence of $T_c$ of MoN thin films with those of NbN thin films, Fig. 2 shows the normalized $T_c$ (i.e. $T_c/T_{c0}$) as a function of $R_{sq}^N$ for both MoN and NbN thin films [9, 13]. Though $T_{c0} = 6.45$ K for MoN thin films is different from that for NbN films 14.85 K, the $\tau = 1.6 \times 10^{-16}$ s for MoN films is also the similar value for NbN films $1.0 \times 10^{-16}$ s. The value of $R_c$ is also similar to that for NbN [16]. The mechanism of SIT for MoN films should be similar to that of NbN films.

We also discuss about the difference of the mean free path $\ell$ between MoN and NbN thin films. We can estimate $\ell$ by three different methods. Two of them use the relation $\ell = v_F\tau$, where the Fermi velocity $v_F$ can be calculated assuming the free electron model $v_F = (\hbar/m)[(3\pi^2)n]^{1/3}$. The elastic scattering time $\tau$ can be estimated from the Drude model (the free electron model) $\tau = m/(ne^2\rho)$ or the fitting parameter of Finkel’stein formula. Therefore $n$ and the resistivity $\rho$ are used in order to obtain the mean free path by the first method $\ell_{\rho} = (\hbar/e^2)[(3\pi^2)/n^{2}]^{1/3}$, while $n$ and $\tau$ are necessary to calculate it by the second method $\ell_{\tau} = (\hbar/m)[(3\pi^2)n]^{1/3}$. The third method is used the relation $\ell_D = 3D/v_F = 3D(m/h)[(3\pi^2)n]^{-1/3}$, where the diffusion constant $D$ can be determined from the slope $H_{c2}-T$ curves near $T_c$, given by $D = (4k_B/\pi\varepsilon)|dH_{c2}/dT|^{-1}$.

The upper critical magnetic field $H_{c2}$ were measured for three typical superconducting films (No. 5, 7 and 8, 4 K < $T_c$ < 5 K) in order to calculated the diffusion constant $D$. Figure 3 shows $T$ dependences of $H_{c2}$ and the fitting lines to obtain the slope. The value of the slope is $|dH_{c2}/dT| = 2.6 \sim 3.0$ T/K, and $D$ is estimated to be 0.37 \sim 0.43 cm$^2$/s. Because the sample dependence of $D$ is not so large, hereafter we use the data for the No. 8 film for simplicity.

The carrier density $n$ for the No. 8 film at $T = 20$ K is about $2.3 \times 10^{20}$ m$^{-3}$, this value is larger than reported values for NbN films ($3.0 \times 10^{28}$ m$^{-3}$ < $n$ < $1.4 \times 10^{29}$ m$^{-3}$) [16]. This discrepancy between MoN and NbN films cannot be understood in the present stage. It was estimated that $\rho$ for MoN films is about 3 $\mu\Omega$m from the relation between $R_{sq}$ and $1/d$ [13]. We can also use the elastic scattering time $\tau = 1.6 \times 10^{-16}$ s from the Finkel’stein fitting parameter and $D = 0.4$ cm$^2$/s for MoN thin films. The calculated mean free paths ($\ell_{\rho}$, $\ell_{\tau}$ and $\ell_D$) are shown in Table 2. There is some differences of $\ell$ for MoN films determined by the different
methods. It may be related to the large value of $n$. Because each formula has the different $n$
dependence as follows: $\ell_\rho \propto n^{-2/3}\rho(n)^{-1}$, $\ell_\tau \propto n^{1/3}\tau(n)$ and $\ell_D \propto n^{-1/3}D(n)$.

For NbN thin films it was reported that $0.1 \text{ nm} < \ell_\tau < 0.2 \text{ nm}$ and $0.1 \text{ nm} < \ell_D < 0.3 \text{ nm}$ [16]. Since $\rho$ for NbN films is about $1 \mu\Omega\text{m}$ [16], it was calculated that $\ell_\rho$ is in the range of $0.5 \sim 1.2 \text{ nm}$. For NbN films the two values ($\ell_\tau$ and $\ell_D$) are nearly equal. However the values of $\ell_\tau$ and $\ell_D$ for MoN films determined in this work are larger than those for NbN films. It is possible that MoN films are more suitable for superconducting devices rather than NbN films from a viewpoint of the mean free path. While $\ell_\rho$ for MoN films is smaller than that for NbN films. These discrepancy should be related with the values of $\tau$ and $\rho$ since $\tau$ calculated from $\rho$ and $n$ for No.8 film is $4.9 \times 10^{-18} \text{ s}$ and is very smaller than $1.6 \times 10^{-16} \text{ s}$. Further investigation needs because the thickness $d$ and other parameters dependence of $\ell$ are not understood.

| materila | $\ell_\rho$ (nm) | $\ell_\tau$ (nm) | $\ell_D$ (nm) |
|----------|-----------------|-----------------|--------------|
| MoN (No. 8) | 0.023 | 0.76 | 2.5 |
| NbN | $0.5 \sim 1.2$ | $0.1 \sim 0.2$ | $0.1 \sim 0.3$ |

4. Summary

We have investigated that the $T_c$ depression and the SIT in MoN thin films. Thin films in the range of $3 < d < 60 \text{ nm}$ were fabricated by DC reactive magnetron sputtering method. It is found that $T_c$ vs. $R_{sq}^N$ data were fitted to the Finkel’stein formula using $T_{c0} = 6.45 \text{ K}$ and $\tau = 1.6 \times 10^{-16} \text{ s}$. The critical sheet resistance $R_c$ is also found about $2 \text{ k\Omega}$, which is smaller
than $R_Q$. The mechanism of SIT for MoN films may be similar to that of NbN films. The mean free path $\ell$ for MoN films is $0.6 \sim 3$ nm, which is larger than that for NbN films. Further studies are needed about the thickness dependence of $\ell$ for MoN films.

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