Grain boundary scattering in the normal state resistivity of superconducting NbN thin films

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NbN films prepared by reactive dc sputtering at high ambient pressure exhibit anomalous normal-state resistivity, as pervasively reported in literature. Most of the prepared films exhibit negative temperature coefficient of resistivity (TCR), while a few films are metallic (TCR > 0) at room temperature and are nonmetallic (TCR < 0) at temperatures between 200 and 300 K. Theoretical fittings by the model of grain-boundary scattering yield a better congruence with the experimental data, than those by exploiting the model of electron localization. This suggests that the transport mechanism of sputtered film prevails manipulated by grain boundary scattering rather than by defect scattering or by impurity scattering.

I. INTRODUCTION

The composition and superconducting properties of NbN films have been extensively studied for more than 20 years. In the meantime, different deposition methods for preparing NbN films, such as chemical vapor deposition, electron gun evaporation, and magnetron sputtering, etc. have been proposed. Among them, the reactive sputtering seems to yield better reproducibility for film properties. A niobium target can be sputtered either in the dc or rf mode of Ar and N\textsubscript{2}. The deposited film contains the fcc \textit{c}-NbN phase possessing a relatively high transition temperature or the hexagonal \textit{e}-NbN phase which is nonsuperconducting until down to 1 K. Usually, the nonsuperconducting phase is comprised of Nb\textsubscript{2}N\textsubscript{y} compounds. For a particular sputtering system, there exists an optimum N\textsubscript{2}-to-Ar pressure ratio to produce the highest \textit{Tc}'s. The Nb\textsubscript{2}N may be found at low nitrogen partial pressure while the \textit{e}-NbN is formed at high N\textsubscript{2} partial pressure. Thus, the parameters of reactive sputtering that influence the formation of various phases are the N\textsubscript{2}-to-Ar pressure ratio, the total sputtering pressure, the purity of gases, and the substrate temperature, etc.

Early results of Gavaler, Keskar, and Shy et al.\textsuperscript{1-3} showed that NbN films with transition temperatures of 14–17 K can be reactively sputtered at substrate temperatures of 300–700 °C and a total pressure below 1.33 Pa. For the proposal of device fabrication, deposition at high substrate temperatures will induce impurity diffusion and is not practical. Later, Bacon et al.\textsuperscript{4} revealed that NbN films can also be prepared at room temperature by reactive dc magnetron sputtering without intentional substrate heating, while its temperature ascent due to charge bombardment during sputtering is estimated to be less than 90 °C. They obtained a maximum \textit{Tc} of 14.2 K for samples prepared in 15% N\textsubscript{2} and 85% Ar with a total pressure of 1.06 Pa. This process is particularly useful for the production of Josephson junctions. Continuous efforts done by Talvacchio and Braginski\textsuperscript{15} demonstrated successful performance of Josephson devices made of NbN films. Recently, Shoji et al.\textsuperscript{6} reported that single crystal NbN films on MgO substrates can be prepared by reactive rf sputtering at an extremely low nitrogen partial pressure and the method yields a \textit{Tc} of as high as 16 K. Besides these, thermal diffusion\textsuperscript{7} of nitrogen into bulk Nb at 800 °C allows \textit{Tc} to increase as high as 16 K, which exhibits lower radio frequency (rf) losses than pure Nb, has also been reported.

With regard to the transport mechanism, Nigro et al.\textsuperscript{8} showed that the negative temperature coefficient of resistivity (TCR) for NbN films could be related to their granular structure. A modified “Drude” model proposed by Reiss et al.\textsuperscript{9} was used to explain this anomalous behavior. However, Pelland et al.\textsuperscript{10} disclosed that NbN films deposited by rf sputtering on MgO substrates revealed a three-dimensional (3-D) weak localization effect as characterized by magneto-resistance measurement. On the other hand, Cabanel et al.\textsuperscript{11} further investigated the transport properties of NbN films deposited by reactive sputtering in a pure nitrogen atmosphere. They studied the variations of resistivity from room temperature to 1 K and showed that the conduction mechanism for films with large resistivity (1–10 mΩ cm) is subjected to thermally activated hopping.

Our aim in this work is not to continue to improve the manufacturing method of NbN films but to clarify the diversified transport behavior of the sputtered NbN films. We investigate the temperature dependence of resistivities of NbN films and try to give a rational explanation relevant to the microstructure of the films.

II. GRAIN BOUNDARY SCATTERING

The model of electrical conductivity of grain-boundary scattering for polycrystalline films was first proposed by Mayadas and Shatzkes.\textsuperscript{12} Two types of electron scattering mechanisms are embraced: an isotropic background scattering due to combined effects of phonons and point defects, and the scattering due to the distribution of planar potential by grain boundaries. From this model, an effective mean free path \textit{Lg} is defined to describe the electron conduction just like ordinary mean free path in the Boltz-
mann conductivity and can easily extend to include the size effect as expressed by the Fuchs–Sondheimer theory.

The dc conductivity of polycrystalline metallic films is suggested to be

\[ \sigma_e = \frac{n e^2 L}{m v_F} \text{grain}(L,D,S), \]  

where \( L \) is the inner-crystalline mean free path describing the volume scattering of the electron, \( v_F \) is the Fermi velocity, \( D \) is the average grain size, and \( S \) is the probability for an electron to pass a single grain boundary. A quantum mechanical calculation of the grain-boundary resistance based on the transfer matrix approach was studied by Reiss et al.\(^7\) On the basis of a great number of experiments, they suggested that the reduction of conductivity depends on the mean probability for electron transmission through the \( L/D \) grain boundaries along one mean free path. The function of \( \text{grain}(L,D,S) \) is the mean value of all transmission probabilities \( T'(i=1,2,3,...J) \) for all possible arrangements of potential arrays along one mean free path. In order to calculate \( T' \), the Hamiltonian

\[ H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \sum_{\xi} V(x-x_{\xi}) \]  

is considered, where \( x_{\xi} \) is the coordinate of grain boundaries and \( V(x-x_{\xi}) \) is the grain boundary scattering potential. If \( J \) is the total number of possible arrangements of potential arrays, then

\[ \text{grain}(L,D,S) = \lim_{J \to \infty} \frac{1}{J} \sum_{i=1}^{J} T'. \]

Based on the experimentally observed features, Hoffman and co-workers\(^1^3\) stated that the reduction of conductivity depends exponentially on the number of grain boundaries per mean free path and all electrons reflected by the grain boundaries along one mean free path do not contribute to the resulting current. Therefore, the conductivity is assumed as

\[ \sigma_e \approx \frac{n e^2 L}{m v_F} S^{L/D}. \]

Under the condition of \( L \ll D \), Eq. (4) reduces to the Drude conductivity without attention to the grain boundary scattering effect. This model predicts a linear behavior of \( \ln[\text{grain}(L,D,S)] \) as a function of \( L/D \), in agreement with experimental data\(^1^3\) for the values of \( L/D > 1 \). Meanwhile, the effective mean free path is given by

\[ L_e = L S^{L/D}, \]

where \( L^{-1} = l_e^{-1} + l_m^{-1} \). Here, \( l_e \) is the elastic mean free path arising from acoustic phonon scattering on the assumption that the conductivity is perfectly metallic within each grain. The temperature dependence of inelastic mean free path \( l_m \) is expressed as\(^1^4\)

\[ l_m^{-1}(T) = \alpha T^\beta \int_0^{\Theta/T} \frac{4x^2 dx}{(e^x-1)(1-e^{-x})} \approx \alpha T^\beta, \]

where \( \Theta \) is the Debye temperature and \( \alpha \) is a proportional constant. In the temperature region of \( T \gg 50 \text{K} \), the value of \( p \) is approximately averaged to be 2–4 depending on the phonon spectrum of the material. By this simplified model, the TCR can be deduced to be

\[ \frac{1}{\rho} \frac{d\rho}{dT} = -\left( \frac{1}{L} + \frac{\ln S}{D} \right) \frac{dL(T)}{dT} = -f(T) \frac{dL(T)}{dT}, \]

where \( \rho_e \equiv 1/\sigma_e \). Since \( dL(T)/dT \) is always negative, the sign of TCR is determined by the function \( f(T) \) in Eq. (6). In the deduction of Eq. (6) we have assumed that the electron transmission probability \( S \) is temperature independent. From Eq. (6), the variation of TCR can be classified into two different kinds when the temperature is down from room temperature. If \( f(T) \) is initially negative, then the sign of TCR will never change as the temperature decreases. However, if \( f(T) \) is positive at room temperature, some critical temperatures may exist at which TCR changes its sign from positive to negative. This critical temperature \( T_m \) can be evaluated by setting \( f(T) = 0 \) and is expressed as

\[ T_m = \frac{\alpha}{l_e} \left( \frac{1}{D} \ln S + 1 \right). \]

Obviously, the metallic to nonmetallic transition of TCR can be readily perspected by this simplified model.

**III. WEAK LOCALIZATION**

The concept of electron localization has been studied for many years and used to explain the temperature coefficient of resistivity for various weakly disordered metallic systems. According to the work of Kaveh and Mott,\(^1^5\) the conductivity in the disordered 3-D system with the quantum correction for the Boltzmann conductivity is obtained. The Hamiltonian of this model is similar to Eq. (2) and the perturbed wave function is expressed by

\[ \phi = \left| k_F \right| + \sum_q \alpha_q \left| k_F + q \right|, \]

where \( \alpha_q \) can be deduced from the diffusion model. The wave function of electrons in such a system includes both extended and localized terms. The reduction of conductivity depends on the coefficients of diffusional wave function. Using the Kubo–Greenwood formulation, we obtain\(^1^6\)

\[ \sigma = \sigma_b (1 - 2R) \]

and

\[ R = \frac{1}{2\pi^2 N(E_F)D} \left( \frac{1}{l_0} - \frac{1}{L_m} \right), \]

where \( \sigma_b \) is the conventional Boltzmann conductivity, \( N(E_F) \) is the density of states at Fermi energy \( E_F \), \( l_0 \) is the elastic mean free path resulting from impurity or defect scattering which is relevant to the localization model, and \( L_m \) is the inelastic diffusion length defined as \( L_m = \sqrt{l_0 l_m/2} \), which is the maximum length for electrons to...
diffuse without being interrupted by an external perturbation. The inelastic mean free path, $l_{in}$, has the same expression as Eq. (5). Synoptically, $R$ represents the probability that an electron diffuses from a state $e^{i(kF+q)r}$ to all other states $e^{i(kF+q)r'}$. Under the condition of weak localization, i.e., $R \ll 1$, the conductivity can be approximated to

$$
\sigma = \sigma_0 \left[ 1 - \frac{3}{(k_Fl_0)^2} \left( 1 - \frac{l_0}{l_{in}} \right) \right]
$$

$$
= \sigma_0 \left[ 1 - \frac{3}{(k_Fl_0)^2} \left( 1 - \frac{l_0}{l_{in}} \right) \right] + \frac{e^2}{\pi \hbar} \left( 1 - \frac{(k_Fl_0)^2}{3l_{in}} \right)
$$

$$
= \sigma_0 + \sigma(T).
$$

In deriving Eq. (10), we assume $l_0 < l_{in}$ which is satisfied by most highly disordered metals at room temperature. The first term represents the zero-temperature, quantum-corrected conductivity $\sigma(0)$ due to localization; the second term $\sigma(T)$ describes the competition between the degradation of the quantum-interference effects as a result of inelastic scattering and conventionally thermal excitation of various inelastic processes. Obviously, the balance between these competing effects on the current-transport of electrons will determine the value of TCR and its sign. The metallic to nonmetallic transition may be estimated by the equation of

$$
I_m(T_m) = \frac{2e^2k_F^4}{9}
$$

It should be noted that Eq. (10) is held only when $l_{in} < l_{in}$. For $k_Fl_0 \approx 1$, the temperature dependent term will be always positive, so the TCR is negative (nonmetallic). However, when $k_Fl_0$ increases, there exists a critical temperature $T_m$ above which TCR will change its sign implying the manifestation of temperature dependence of metallic conductivity.

From the above discussions, the anomalous properties of electron transport in NbN films seem to be able to be explained by either the grain-boundary scattering or the 3-D weak localization. We attempt to elucidate the most probable mechanism with the theoretical analysis of the experimental data by using the fitting method of least-square error.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$P_{Ar}/P_{N_2}$</th>
<th>$T_{sub}$ (°C)</th>
<th>Annealing</th>
</tr>
</thead>
<tbody>
<tr>
<td>S118</td>
<td>10/1</td>
<td>5.06</td>
<td>200</td>
</tr>
<tr>
<td>S119</td>
<td>10/1</td>
<td>5.06</td>
<td>200</td>
</tr>
<tr>
<td>S702</td>
<td>9/1</td>
<td>12.6</td>
<td>400</td>
</tr>
<tr>
<td>S712</td>
<td>9/1</td>
<td>12.6</td>
<td>500</td>
</tr>
<tr>
<td>S722</td>
<td>9/1</td>
<td>12</td>
<td>500</td>
</tr>
<tr>
<td>S724</td>
<td>9/1</td>
<td>12</td>
<td>600</td>
</tr>
<tr>
<td>S108</td>
<td>9/1</td>
<td>8.93</td>
<td>400</td>
</tr>
<tr>
<td>S827</td>
<td>8/1</td>
<td>12</td>
<td>400</td>
</tr>
<tr>
<td>S9D19</td>
<td>8/1</td>
<td>12</td>
<td>80</td>
</tr>
</tbody>
</table>

*Table I. Deposition conditions of sputtered NbN films.

**Sample without intended substrate heating.

**Samples without post-thermal annealing.

IV. SAMPLE PREPARATION AND CHARACTERIZATION

NbN films deposited on Si substrates by reactive dc sputtering at high sputtering pressure are implemented in this transport study. The background pressure before sputtering is less than $1.33 \times 10^{-3}$ Pa which is attained by a turbomolecular pump. In this system, two independent needle valves control the fine adjustment of the $N_2$-to-$Ar$ ratio which is within the range from 1/8 to 1/10 of a total sputtering pressure being greater than 1.33 Pa. The dc high voltage is kept at 3.5 kV and the substrate temperature is heated from room temperature to 600°C. Experimentally, too small total sputtering pressure or dc high voltage will cause a very low sputtering rate. The temperature dependence of resistivity and the superconducting transition temperature are measured by the standard four-point-probe method and the film thickness is determined by the cross-sectional view of scanning electron microscopy (SEM). As for the crystal structure and the microstructure of films are determined by x-ray diffraction and a transmission electron microscopy (TEM), respectively. Additionally, the depth composition profiles of the films are analyzed by an Auger electron spectroscopy (AES).

Deposition conditions for several sputtered films have been documented in Table I. From the ring pattern of transmission electron diffraction, the microstructure of the NbN films is polycrystalline and can be categorized into fine randomly oriented grains. For example, we consider the case that the pressure ratio of $N_2$ to Ar is kept at 1/9.

FIG. 1. TEM photographs of the NbN films showing the microgranular structure. (A) S722, (B) S724, (C) S108.
The TEM photographs, as shown in Fig. 1, reveal that these films are granulated and surrounded by voids or other amorphous material with an average grain size of the order of 20 nm. Larger grain sizes between 30 and 40 nm can be obtained by post thermal annealing or sputtered at lower pressure. Although the latter seems to yield larger grain sizes, the separation between grains appears to be larger. This implied a weak intergrain coupling.

The crystal structure and its phase investigated by x-ray diffraction are shown in Fig. 2. All analyzed films exhibit diffraction peaks belonging to the fcc B1 structure and the peaks of (111) and (200) of $\delta$-NbN phase have been identified. As usual, the intensity of the (200) peak is stronger than that of the (111) peak except for the thermally annealed films. In particular, the trace for sample S724 (post-annealed film) shows an asymmetric (111) peak, likewise sample S827 ($P_{N_2}/P_{Ar} = 1/8$) has an asymmetric (200) peak. Indeed, when a polycrystalline metal film is deformed elastically, the lattice plane spacings in the constituent grains change from their stress-free values. On the other hand, if the metal is deformed plastically, the lattice planes become distorted and cause the unsymmetric broadening of the x-ray diffraction line. The fast quench of the post annealing and the forming of multiphase oxidize— and carbonitride niobiums may introduce stress in NbN films and result in lowering the $T_c$. These suggestions are supported by the observation of TEM and AES spectra.

In Table II the average compositions of the samples are examined by AES. It can be seen that the content of $N_2$ is the smallest for the samples deposited at a pressure ratio of $N_2/Ar$ being $1/9$, which is hardly changed by substrate heating or thermal annealing. Since the dc voltage of 3.5 kV is kept through the experiments, a constant content of 48% Nb is obtained. Accompanying Nb loss, the carbon (C) impurities in the sample are largely increased after thermal annealing, which may be introduced from chamber contamination at high temperatures. The high contents of carbon as examined by Auger spectrometry indicate that the films may be contaminated by niobium carbonitride. We find that the highest $T_c$ occurred when the pressure ratio of $N_2$ to Ar is $1/9$, although the content of $N_2$ is the smallest. The characteristics of some NbN films are listed in Table III in which we choose those samples showing distinguishable resistivity-to-temperature traces as depicted in Fig. 3. These experimental results are close to those reported in Ref. 11.

The sputtered films with thickness of 50–120 nm are characterized with high resistivity ($>1$ m$\Omega$-cm). The transition temperature $T_c$, has a range from 5 to 12 K and the $\Delta T_c$ reduces from 1.5 to 0.25 K as $T_c$ increases. The films with smaller contents of carbon or with lower $R_{res}$ seem to have higher $T_c$. The increase of $\Delta T_c$ may be at-

![FIG. 2. X-ray diffraction patterns of NbN films. The peak of Si(100) at 2θ≈33° is also shown as a reference.](image-url)
TABLE III. Experimental data of superconducting transition temperature $T_c$, the temperature difference $\delta T_c$ between $T_c$ and the on-set temperature $T_{co}$, the resistivity $\rho_{co}$ at $T_{co}$ and the residual resistivity ratio.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (nm)</th>
<th>$T_c$ (K)</th>
<th>$\delta T_c$ (K)</th>
<th>$\rho_{co}$ (m$\Omega$ cm)</th>
<th>$\rho_{RT}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S712</td>
<td>119.9</td>
<td>5.35</td>
<td>0.85</td>
<td>13.3</td>
<td>0.735</td>
</tr>
<tr>
<td>S702</td>
<td>49.6</td>
<td>6.8</td>
<td>0.56</td>
<td>5.74</td>
<td>0.625</td>
</tr>
<tr>
<td>S724</td>
<td>52.1</td>
<td>8.26</td>
<td>1.59</td>
<td>3.3</td>
<td>0.303</td>
</tr>
<tr>
<td>S108</td>
<td>49.5</td>
<td>10.8</td>
<td>0.37</td>
<td>2.65</td>
<td>0.714</td>
</tr>
<tr>
<td>S722*</td>
<td>80.3</td>
<td>11.73</td>
<td>0.25</td>
<td>1.71</td>
<td>0.5</td>
</tr>
</tbody>
</table>

*Samples exhibit resistivity minimum at $T_{m}=200-300$ K.

V. DISCUSSIONS

The unexpected smallness of the elastic mean free path $l_0$ and the vast difference of $l_0$ in the same batch of samples simulated from the localization mechanism imply that the transport mechanism of the sputtered NbN films can be elucidated more fully by the grain boundary scattering than by the 3D weak localization. Our previous work on the analysis of ultrathin films of $Y_1Ba_2Cu_3O_{7-\delta}$ superconductors also showed the same approach. As pointed out by Kaveh and Mott, the localization picture deals with electron wave functions separated by an energy difference $\hbar \tau_1^{-1}$, which are nearly equal for all degenerate states, where $\tau_1$ is the temperature dependent inelastic scattering time.

The electrons are allowed to diffuse thermally until an inelastic scattering takes place. Thus, the interval $\hbar \tau_1^{-1}$ between the energy levels is much less than $k_B T$. If $k_B T > \hbar \tau_1^{-1}$, then the weak localization model is not applicable. So, weak localization is usually limited to the low temperature region (i.e., $l_0<<l_0$) and only applicable for the slow variation of TCR. For the NbN films, the TCR is even negative at high temperature ($T>200$ K) and the resistivity ratio of $R_I/R_{RT}$, where $R_I$ is the resistance at some specified temperature $T$, may be greater than 2. This result indicates that the 3-D weak localization effect is not pertinent to these films. For the validity of weak localization, the changes of conductivity within the temperature range of 0–300 K must be generally 10% less than its values at $T_{co}$. This tacit assumption is supported by the
TABLE IV. Typical parameters obtained for best fitting with theories of 3D weak localization (see Ref. 15) and grain boundary scattering (see Ref. 19).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$p$</th>
<th>$l_0$ (nm)</th>
<th>$k_F$ (nm$^{-1}$)</th>
<th>$l_m$ (nm)</th>
<th>$T^{-p}$</th>
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<tr>
<td>S108</td>
<td>3</td>
<td>0.35</td>
<td>6.12</td>
<td>4.073 x 10^6</td>
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</tr>
<tr>
<td>S724</td>
<td>3</td>
<td>0.12</td>
<td>15.4</td>
<td>4.653 x 10^7</td>
<td></td>
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<tr>
<td>S722</td>
<td>3.25</td>
<td>0.12</td>
<td>16.6</td>
<td>8.778 x 10^7</td>
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<table>
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<tr>
<th>Sample</th>
<th>$p$</th>
<th>$l_0$ (nm)</th>
<th>$k_F$ (nm$^{-1}$)</th>
<th>$l_m$ (nm)</th>
<th>$D$ (nm)</th>
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<tbody>
<tr>
<td>S108</td>
<td>2.5</td>
<td>52</td>
<td>1.043 x 10^6</td>
<td>40</td>
<td>0.23</td>
<td></td>
</tr>
<tr>
<td>S724</td>
<td>2.5</td>
<td>40</td>
<td>2.901 x 10^7</td>
<td>30</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>S722</td>
<td>3</td>
<td>32.5</td>
<td>3.310 x 10^8</td>
<td>25</td>
<td>0.12</td>
<td></td>
</tr>
</tbody>
</table>

results of theoretical fitting. As specified in Table IV (top), all samples indicate very short elastic mean free path $l_0$ satisfying $k_F l_0 \approx 1$, which implies weak localization being not justified. As shown in Fig. 4, the fitting with Eq. (10) for the film of S722 is poor and, at the same time, it seems to be difficult to explain the phenomena of TCR transition at high temperatures and the saturation of resistivity at low temperatures by the weak localization effect.

On the other hand, the grain-boundary scattering offers a more acceptable fitting parameters for the negative TCR of NbN films even for samples (e.g., sample S722) with exotic bumps as shown in Fig. 3. The resistivity saturation has also been predicted successfully. In exploiting Eq. (4), we assume that $D/L < 1$ and the electron density $n$ and the transmission probability $S$ are temperature independent. The temperature dependence of inelastic mean free path is expressed by Eq. (5). At high temperatures ($T > 200$ K), the exponent $p$, dominantly controlled by electron-phonon scattering, is near the order of unity and increases to 2–5 for $T$ below 40 K. In order to simplify the complexity of fittings, the value of $p$ is presumed to be fixed in the range of 2–4 in the temperature region which we are concerned about. As shown in Fig. 3, the large fitting error spanning at $T < 50$ K may be attributed to this simplification. The average grain sizes from 20 to 40 nm are estimated from the TEM diagrams as shown in Fig. 1. The best fitting result shows that the average electron density $n$ is in the magnitude of $10^{21}$ cm$^{-3}$ and the electron transmission probability $S$ is in the order of $10^{-1}$ which is close to the value cited by Reiss et al. but is much larger than that obtained by Nigro et al. (of $10^{-5}$–$10^{-10}$).

Oxidized surfaces of NbN are shown to be NbN$_{1-x}$O$_x$-N$_2$O$_3$ overlayers which shall depress the conduction between grains by revealing small transmission coefficients $S(<0.1)$. The large discrepancy of $l_m$, as established in Table IV, truly reflects the vast difference of composition and structure for samples obtained by a slight modification of deposition procedures.

In conclusion, NbN films reactively sputtered on Si substrates at high pressure preserve most of the same transport characteristics as those sputtered at low pressure. The samples prepared under this experimental condition have a

FIG. 4. The best fitting of resistivities vs temperature with the 3D weak localization equation of the same samples.
highest transition temperature of 12 K and show a negative TCR at normal state. Lower \( T_c \) may result from the proximity effect and the existence of impurities. The normal state resistivity can be well explained by the model of grain-boundary scattering rather than by weak localization, particularly at high temperatures. The best fitting result implies that the inelastic scattering mean free path seems to be a much more complicated power-law-function of temperature that what we have adopted as a simple constant.

For a dirty superconductor, McMillan derived the general formula of critical temperature \( T_c \) under strong coupling²

\[
T_c = \frac{\theta_D}{1.45} \exp \left( \frac{-1.04 \left[ 1 + \lambda(\rho) + y(\rho) \right]}{\left[ \lambda(\rho) - \mu^*(\rho) \right] \left( 1 + \frac{0.62 \lambda(\rho)}{1+y(\rho)} \right)} \right),
\]

where \( \rho \) is the extrapolated resistivity which serves as a measure of disorder, \( \theta_D \) is the Debye temperature, \( \lambda(\rho) \) and \( \mu^*(\rho) \) are the generalized electron-phonon coupling constants and Coulomb pseudopotential, and the additional renormalization function \( y(\rho) \rightarrow 0 \). In the presence of disorder, interplay between the electron-electron interaction and the disorder give rise to novel effects, which lead to a suppression of the density of states at the Fermi level, and consequently the \( T_c \). In weak disorder and with the neglect of the Coulomb term, Eq. (12) can be roughly simplified to yield the deviation of critical temperatures²³

\[
\delta T = \frac{T_c - T_c(\rho=0)}{T_c(\rho=0)} = \frac{\rho}{\rho_M} \times \frac{1.04}{\lambda} (a - b\lambda),
\]

where \( a \) and \( b \) are some constants, \( \rho_M \) is the Mott resistivity which is of the order of 1000 \( \mu \Omega \) cm. This equation shows that \( \delta T \) is large and positive for lower \( T_c(0) \), and small and negative for high \( T_c(0) \). Table III readily reflects this approach. This table also reveals that the superconducting transition temperature decreases with \( \rho_{\text{res}} \), indicating that the disorder or the grain tunneling is crucial to the superconducting state.

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