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Effect of Interstitial Impurities on the Residual Resistivity of Niobium Thin Films

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Effect of Interstitial Impurities on the Residual Resistivity of Niobium Thin Films

A thesis submitted in partial fulfillment of the requirement for the degree of Bachelors of Science in Chemistry from The College of William and Mary

by

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(Honors, High Honors, Highest Honors)

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April 28, 2008
Abstract

The favorable superconductive properties of niobium have led to its extensive use in superconducting radio frequency (SRF) linear accelerator cavities. In order to reduce the cost of these cavities, while at the same time developing avenues by which their properties can be enhanced, substantial effort has been directed towards developing high quality Nb/Cu thin film cavities to replace conventional bulk Nb cavities. The properties of superconducting Nb thin films are still not completely understood; however, substantial evidence exists suggesting that these properties are significantly affected by thin film purity. Thin films (~300nm) were deposited via physical vapor deposition using as-received (99.9% pure) and electrotransport purified niobium source rods. Multiple surface analysis techniques (Auger electron spectroscopy, X-ray photoelectron spectroscopy, energy dispersive X-ray spectroscopy) were utilized to characterize the thin film purity, while residual resistance ratios were determined for the films using the four-point-probe method at room temperature down to 10K ($T_c$ for Nb ~ 9.3K) as a means of measuring their superconducting quality. It was found that a significant CO partial pressure inherent to the physical vapor deposition method employed obscured the gain in purity between the as-received and electrotransport purified films. However, it was clear from residual resistivity ratio measurements of an electrotransport-purified sample compared with values reported in the literature that there is a significant gain in superconductive quality when electrotransport purification is performed. Since the carbon and oxygen impurity level deposited into the thin films is very clearly an issue of related rates, future studies would require high temperature electron evaporation, such as that obtained using a high-temperature Knudsen cell, to increase the Nb deposition rate with respect to the deposition of residual impurity gases present in the system during film nucleation and growth. This would lead to improved thin film purity and thus, enhanced superconductive quality of the deposited films.
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1. **Introduction**

Over the past twenty years, a significant effort has been directed to developing superconducting niobium thin films as a replacement for bulk niobium superconducting radio frequency (SRF) cavities. Niobium is an attractive superconducting material due to it having the highest \( T_c \) (9.3K)\(^1\) and the highest \( B_{c1} \) (~170mT at 2K) of any pure metal\(^2\). The critical temperature (\( T_c \)) is the temperature at which a material enters a superconducting state and \( B_{c1} \) is the external magnetic flux density at which magnetic field lines are first able to penetrate the superconductor’s surface. \( B_{c1} \) is a particularly important property since it dictates the maximum accelerating field possible for a given cavity, which for bulk niobium is approximately 40-50 MV/m. Due to the ever-increasing demand for higher accelerating fields, the critical field is often approached in many single and multiple cell bulk niobium SRF cavities in use today. Despite the well-established utility of bulk niobium cavities, the general consensus in the scientific community is that barring some major discovery, bulk cavities have reached the upper limit of performance\(^3\). Because of this, researchers have spent a great deal of effort in developing superconducting niobium thin film deposition techniques that will eventually allow them to circumvent the cost and physical limitations of bulk niobium cavities.

Two major advantages of niobium thin film SRF cavities, especially those coated on copper, are the high thermal conductivity, or resistance to quench – the breakdown of the accelerating field present in the cavity – and the significantly reduced cost of materials\(^4\). A deposition technique that will yield consistent material properties, especially with respect to microstructure uniformity\(^{1,4,5}\) and low film impurities\(^{5,6}\) is of great interest. However, little attention has been paid to the impurities present in the
niobium source used for deposition and to the background contamination of the vacuum system during deposition. This lack of attention is especially surprising considering the compelling evidence\textsuperscript{[1,6]} suggesting this may be a significant factor inhibiting the superconducting performance of Nb thin films as defect density\textsuperscript{[4,5]}. The final impurity concentration present in the deposited film is a function of the source material purity and the environment during deposition. In other words, a deposited film can only be as pure as the material from which it is being deposited and the uptake of impurities during deposition. Therefore, if a method could be devised to ultrapurify the source niobium and to conduct deposition in the most pristine environment possible, a significant improvement in superconducting properties would be observed. It has been shown that the electrotransport purification of thorium, an actinide metal capable of superconduction, conducted in ultrahigh vacuum conditions resulted in a two order of magnitude increase\textsuperscript{[7]} in the residual resistivity ratio (RRR) – the metric by which superconducting quality is assessed. Thus, electrotransport purified niobium metal used as a deposition source in an ultrahigh vacuum environment may significantly reduce impurities present in the deposited film, which in turn may substantially increase RRR values of Nb/Cu thin films compared to those previously achieved.

1.1 Superconducting Radio Frequency (SRF) Bulk Niobium Cavities

The majority of high-accelerating gradient linear accelerators (linacs) are constructed using bulk niobium SRF cavities\textsuperscript{[1]}, e.g., the Continuous Electron Beam Accelerator Facility (CEBAF) at Jefferson Lab in Virginia, and Fermilab in Illinois.
1.1.1 Linear Accelerators

The basic principle of acceleration in a SRF linac is as follows. Electrons (or particles) that have already been accelerated to some fraction of the speed of light are injected into the linac cavity. An RF field is then applied linearly down the accelerator cavity so that the injected electrons are collimated in such a way that their scattering off of the walls of the cavity is minimized. This field has both an accelerating and decelerating effect depending on the phase of the RF field the electrons experience at any given moment. The interaction of the electrons with the field in the kth frequency domain is described by the characteristic cavity impedance \( (R/Q)_k \), where \( R \) is the shunt impedance and \( Q \) is the quality factor, according to the equation:

\[
(R/Q)_k = \frac{|V_k|^2}{\omega_k W_k}
\]

where \( \omega_k = 2\pi f_k \) and \( W_k \) are the angular frequency and stored energy, respectively, of the kth mode of the field and where \( |V_k| \) is the amplitude of the voltage experienced by the particles as they move down the linac\(^8\). The cavity itself is shaped in such a way as to expose the electrons in phase with the accelerating portion of the field and shield them from the decelerating field, thus constantly accelerating the electrons linearly down the length of the linac. When the electrons reach the end of the linac, they have been accelerated to relativistic speeds close to the speed of light and are then channeled to regions for various applications.

SRF cavities for use in linacs employ a multi-cell resonator structure in order to achieve high accelerating gradients for particle acceleration. Multi-cell cavities can have anywhere between 5 and 9 resonator cells and are cylindrically symmetric with an
elliptical shape having been found to be the optimal geometry\[9\]. As seen in Figure 1.1, the magnetic and electric fields produced inside a nine-cell cavity yield extremely favorable conditions for accelerating electrons through the cavity. The contours show the magnetic field directs the electrons straight through the axis of symmetry of the cavity (inhibiting dispersion), and the electric field created by the RF source is strong inside the cavity when in the accelerating mode and weak inside the cavity when in the decelerating mode, yielding linear acceleration. Since the performance of these cavities relies on the conductivity of the material from which they are constructed, a cavity made of a superconducting material is obviously desirable, hence the use of niobium in such systems.

1.1.2 Quality and Performance of SRF Cavities

The overall quality and performance of SRF cavities is measured using three standards: residual resistance ratio (RRR) values – which are a measure of the overall quality of the material being used, quality factors ($Q_0$) and accelerating gradient ($E_{\text{acc}}$). The RRR values are determined using a four-point probe method in which the resistance of the material at room temperature is compared to the resistance at 4.2K as given by the equation:

$$\text{RRR} = \frac{R_{300K}}{R_{4.2K}} \approx \frac{\rho(300K)}{\rho(4.2K)} = \frac{\rho_{\text{phonons}}(300K) + \rho_{\text{defects}}}{\rho_{\text{phonons}}(4.2K) + \rho_{\text{defects}}}$$

(1.2)
where \( \rho(T) \) is the resistivity of the niobium at a given temperature \( T \). This measure is useful in that it gives a measure of the electron conductivity of the superconducting material, since as indicated in Equation 1.2, the resistance is a function of the temperature-independent resistivity caused by defects \( (\rho_{\text{defects}}) \). To date, the defect density has focused on structural defects such as point (vacancies), line (dislocations), areal (grain boundaries, stacking faults) and volume (porosity) disorder.

Typically the quality factor is measured as a function of the stored energy in the cavity versus the power dissipated by residual surface resistance. Quality factor \( (Q_0) \) is defined by the equation:

\[
Q_0 = \frac{\omega W}{P_{\text{diss}}}
\]  

(1.3)

where \( P_{\text{diss}} \) is the power dissipated as a function of residual surface resistance \( (R_{\text{surf}}) \) and \( W \) is the energy stored in the electromagnetic field in the cavity. This relationship can then be rearranged to the following equation in order to make measurement of \( Q_0 \) more manageable experimentally:

\[
Q_0 = \frac{G}{R_{\text{surf}}}
\]  

(1.4)

where \( G \) is the geometrical constant defined by the geometry of the specific cavity and field distribution of the excited mode according to the relationship:

\[
G = \frac{\omega \mu \int H^2 dV}{\int \frac{\delta}{\lambda} H^2 dA}
\]  

(1.5)

where \( H \) is magnetic intensity, \( \mu \) is permeability, \( V \) is volume and \( A \) is surface area. The factor \( Q_0 \) is extremely important in evaluating superconductive performance since it is a
measure of the cavity’s ability to store energy within an oscillating electromagnetic field. Typical \( Q_0 \) values for SRF cavities lie in the range of \( 10^9 - 10^{10} \) for bulk cavities at lower accelerating gradients\(^4\).

A final way in which cavity performance is conventionally judged is by the accelerating gradient they are capable of achieving. Accelerating gradient (\( E_{\text{acc}} \)) is defined according to the relation:

\[
E_{\text{acc}} = k_e \sqrt{\frac{P_{\text{dis}} Q_0}{\omega}}
\]

where \( k_e \) is a proportionality factor that depends on the geometry of the cavity\(^10\). The maximum accelerating field is limited by the critical RF magnetic field, which is usually somewhere between the \( B_{c1} \) and \( B_{c2} \) of the cavity material\(^11\). Typically as the maximum \( E_{\text{acc}} \) for a cavity is approached, one observes a drop in \( Q_0 \) leading up to cavity quench. Of the three properties listed above (RRR, \( Q_0 \) and \( E_{\text{acc}} \)), \( E_{\text{acc}} \) is the most important because it is the driving force for cavity design. Cavities are designed to maximize the accelerating gradient in order to efficiently achieve maximum particle acceleration (i.e. having to use fewer cavities to achieve the same result).

### 1.1.3 Limitations of Bulk Technology

Good Nb bulk technology results have been achieved for high gradient acceleration at low applied RF fields; however, this technology is fast approaching its theoretical limit. As shown in Figure 1.2, the current world record for accelerating gradients achieved by bulk Nb cavities is approximately 52 MV/m, which is very close to the theoretical limit of 57 MV/m for Nb SRF cavities\(^3,11\), and in most cavities in use today the critical field for Nb (~170mT at 2K) is often approached. This limits accelerating gradients to about 40 MV/m for most SRF linacs. Although the parameters
of $E_{\text{acc}} \sim 40 \text{ MV/m}$ with $Q_o \geq 10^{10}$ are within the acceptable limits for current endeavors such as the International Linear Collider (ILC)\cite{1}, they are at the very far end of the applicability of bulk Nb SRF cavities. Because of this, a revolution in the materials available for use in SRF linacs is necessary in order to construct more efficient cavities with higher acceleration gradients. Thin film cavity technology provides an avenue by which this revolution can take place since it allows for the use of materials from which it would be impossible to construct a bulk cavity.

In addition to the physical limitations, there are several practical issues with bulk Nb SRF cavities. One of the biggest drawbacks is that they are difficult and expensive to fabricate, making large-scale implementation a difficult and costly process. In addition, bulk Nb cavities have poor thermal conductivity, leading to a problem called localized quench\cite{12}. An RF current produces a lot of heat, which is usually dissipated in superconducting Nb to the surrounding liquid He. Localized quenching occurs when there is a small normal-conducting impurity present in the niobium surface. This impurity can lead to very large heating due to a factor of $10^6$ increase in the resistance between a normal conductor and a superconductor\cite{12}. Bulk Nb cannot conduct the heat away quickly enough to the surrounding liquid He and, as a result, a small defect can lead to large-scale heating as more of the material in the cavity becomes normal-conducting and

![Figure 1.2: Highest observed accelerating fields for low loss (LL) and reentrant (RE) bulk Nb cavity designs achieved at the High Energy Accelerator Research Organization (KEK) in Japan, and Cornell\cite{3}](image-url)
heats up, potentially causing quench for the whole system. Figure 1.3 illustrates this effect. Improved materials processing has led to a decrease in this effect; however, further innovation is necessary to completely eliminate this problem and increase cavity efficiency.

Although there are still innovations to be made in the realm of bulk Nb cavities, these lie primarily in quality control and assurance, and industrial process cost optimization. This is not to say that these are trivial problems to overcome; however, any dramatic changes in SRF linac cavity performance must inherently come from other realms of investigation.

### 1.2 SRF Niobium/Copper Thin Film Cavities

Because of these limitations, developing SRF cavities based on niobium/copper thin films as a means to achieve improved accelerator properties while lowering cost is a
priority. The successful launch of the upgrade to the Large Electron-Positron Collider (called LEP-II) at CERN in 1998 \cite{13} proved the viability of thin film technology in particle accelerators and as a result there has been a great thrust towards designing better and purer cavities with higher values of RRR, $Q_0$ and maximum $E_{\text{acc}}$.

1.2.1 Advantages of Nb/Cu Thin Film Cavities

There are many advantages to switching to SRF cavities based on Nb/Cu thin film technology. First and foremost is the substantially lower cost of high-purity copper compared with niobium and the associated lowered machining costs\cite{1}. Copper substrates also have one large advantage over niobium: increased thermal conductivity. Copper effectively eliminates this aspect of the quenching problem since it can move heat to the external liquid He much more efficiently. Additionally, it has been shown experimentally that superconductive behavior in bulk Nb cavities is determined within the penetration depth, i.e. the first 40 nm of the surface, since the electromagnetic field can only penetrate approximately 30nm into the Nb surface\cite{1}. This means that thin films lose none of the superconductivity of bulk niobium as long as they are sufficiently thick. Another advantage to the Nb/Cu thin film technology is the applicability to other superconducting materials with more desirable properties (higher $T_c$, $B_{c1}$, etc…)\cite{4} from which it is more difficult to create bulk cavities. Table 1 gives a few examples of potentially useful alternatives to elemental niobium films and their superconductive properties. Before such technology can be implemented, however, technical challenges facing traditional Nb/Cu technology must first be addressed.
Table 1: Examples of alternative superconducting materials for use in thin film SRF cavities. $H_{c1}$ is the first critical flux as explained earlier, while $H_{c2}$ is the critical external magnetic flux at which superconductivity is destroyed. $\lambda(0)$ is the mean free path of electrons in the superconductor.

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_c$ (K)</th>
<th>$\rho_{n}(\mu\Omega\text{cm})$</th>
<th>$H_{c1}(0)$ [T]</th>
<th>$H_{c2}(0)$ [T]</th>
<th>$\lambda(0)$ [T]</th>
<th>$\lambda(0)$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb</td>
<td>9.2</td>
<td>2</td>
<td>0.2</td>
<td>0.17</td>
<td>0.4</td>
<td>40</td>
</tr>
<tr>
<td>NbN</td>
<td>16.2</td>
<td>70</td>
<td>0.23</td>
<td>0.02</td>
<td>15</td>
<td>200</td>
</tr>
<tr>
<td>NbTiN</td>
<td>17.5</td>
<td>35</td>
<td>0.03</td>
<td>0.03</td>
<td>151</td>
<td></td>
</tr>
<tr>
<td>Nb$_3$Sn</td>
<td>18</td>
<td>20</td>
<td>0.54</td>
<td>0.05</td>
<td>30</td>
<td>85</td>
</tr>
<tr>
<td>$V_3$Si</td>
<td>17</td>
<td>15</td>
<td>0.43</td>
<td>0.03</td>
<td>3.5</td>
<td>140</td>
</tr>
<tr>
<td>Mo$_3$Re</td>
<td>15</td>
<td>0.43</td>
<td>0.03</td>
<td>3.5</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>MgB$_2$</td>
<td>40</td>
<td>0.43</td>
<td>0.03</td>
<td>3.5</td>
<td>140</td>
<td></td>
</tr>
</tbody>
</table>

### 1.2.2 Current Status of Thin Film Technology

Currently, there are several methods being investigated to make Nb/Cu SRF cavities a more viable alternative to bulk Nb SRF cavities. CERN and Accel/Cornell are studying niobium coatings using traditional magnetron sputtering, and have recently implemented a bias mechanism to try to improve the coating qualities. Initial results from CERN have showed an improved surface smoothness at certain applied bias voltages, however no increase in RF performance has been observed to date. Beijing University has been working on biased magnetron sputtering for several years. The copper quarter wave resonator there has reached 4-5 MV/m at 4.2 K with $Q_0$ close to $10^9$. Biasing of the substrate did improve the film quality, but the process has yet to reach its full potential.

In a separate research direction, the Instituto Nazionale di Fisica Nucleare Roma 2 (INFN/Roma2) and Soltan Institute have started a joint venture to investigate niobium coatings using the cylindrical vacuum arc process. The improvement of the thin film quality was dramatic, with RRR values as high as 80 and a bulk-niobium-like $T_c$ observed even for films as thin as 100 nm. The high vacuum conditions are generally considered the main reason for the good film quality, lending strong evidence that film purity plays a
large role in film quality. Although macroparticles on the surface of the film remain a concern for this cavity deposition process, a filter is currently under development to reduce this effect.

Another endeavor at Jefferson Lab has developed an electron cyclotron resonance (ECR) plasma coating system to investigate how the deposition energy can influence the film growth to achieve a thin film with bulk niobium like material properties\textsuperscript{[16]}. The process has all the advantages of the vacuum arc process with the added benefit of a relatively narrow energy span for the fully ionized niobium atoms comprising the deposition flux. The resulting films achieved RRR of 50 and $T_c$ close to that of bulk niobium, and the high deposition energy helped to produce improved crystal orientation for niobium films grown on copper. Due to the limitations of niobium volume in the electron gun hearth, the current sample system is limited to films no thicker than 300 nm.

Table 2 summarizes the recent results from different niobium coating processes.

<table>
<thead>
<tr>
<th>Coating processes</th>
<th>$T_c$(K)</th>
<th>$\Delta T_c$(K)</th>
<th>RRR***</th>
<th>Crystallization (measured by X-ray diffraction)</th>
<th>Film structure by XTEM analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetron Sputtering</td>
<td>9.5</td>
<td>0.3</td>
<td>5-10</td>
<td>Range from oriented to less oriented, depends on deposition angle.</td>
<td>Columnar growth</td>
</tr>
<tr>
<td>Biased Magnetron Sputtering</td>
<td>9.6</td>
<td>&gt;1K</td>
<td>7-15</td>
<td>N/A</td>
<td>Columnar growth</td>
</tr>
<tr>
<td>Vacuum Arc Deposition*</td>
<td>9.25</td>
<td>&lt;0.02</td>
<td>20-100</td>
<td>Preferred orientation, other orientations exist</td>
<td>Columnar growth, densely packed</td>
</tr>
<tr>
<td>Energetic vacuum deposition*</td>
<td>9.1</td>
<td>0.07</td>
<td>50</td>
<td>Perfectly oriented</td>
<td>Epitaxial in some films.</td>
</tr>
</tbody>
</table>

\* $T_c$ measured by different method.

\** Samples made at deposition energy around 123 eV on sapphire substrates.
1.2.3 Technical Challenges

Although promising, Nb/Cu technology faces several important technical challenges. These challenges fall into two main categories: defect density and impurity defects. The current niobium thin films coated in magnetron sputtering systems show columnar structure, which is totally different from the large grain structure found in solid niobium. As shown in the exaggerated depiction in Figure 1.4, a columnar grain structure creates problems in both categories, allowing for significant inclusion of oxide impurities in voids along with increased defect density in the films. As stated earlier, research is currently underway by many groups across the world to solve this problem and optimize surface morphology, [1,4,5,6,15,16] representing only a small portion of what is being done. There are two main sets of theories explaining the possible causes for the high field Q-drop that has plagued Nb/Cu thin films since they were first developed.

Q-drop is defined as the drop in the value of $Q_0$ as the accelerating field is increased in a SRF linac cavity and is an issue that could be explained by many things – columnar film structure being only one of them. Figure 1.5 shows an example of Q-drop in multiple Nb/Cu thin films produced at CERN. There are many theories explaining the underlying cause of this phenomenon – some pointing to defect density being the main cause$^4$, others pointing to film purity being the dominant effect$^{[1,6]}$. The proponents of the idea that defect density is the main cause of Q-drop usually claim one of two things:

![Figure 1.4: Columnar film structure$^5$. Voids and open boundaries lead to increased defect density along with oxide inclusion in the deposited film.](image)
that conductive losses occur across grain boundaries, or increased grain boundary density leads to easier penetration of Josephson fluxons – circulating supercurrents caused by magnetic field penetration – into the superconductor surface\[^4\], which then act as scattering centers for the electron superfluid and increase resistivity. High temperature annealing can reduce the grain density, but is not practical for a copper substrate since it has a low melting point relative to Nb (1358K vs. 2730K). One way to achieve film structure close to that of bulk niobium is to increase the surface adatom mobility while the film grows\[^17\] and there is research currently underway trying to optimize this process. The proponents of the idea that impurity effects are the driving force argue that electron mean free path is the dominant effect in the film surface and that shortened mean free path leads to an increase in the “Q-slope” – the effect that defines the extent of Q-drop\[^1\]. Reduction of impurities would, therefore, increase the mean free path in the superconductor surface and lead to reduced residual resistance\[^6\].

Another piece of evidence suggesting impurities dominate comes from a study done by Wolf et al. demonstrating epitaxial growth of Nb thin films on single crystal Al\(_2\)O\(_3\)\[^18\]. Epitaxial growth means that the films are single crystals of niobium, which in turn means that there are minimal line, areal or volume defects present. In spite of this fact, the films grown in this study reported only moderate RRR values, the highest of
which was 87. These numbers, when compared to a value of RRR=452 reported for 99.9999% pure Nb provided by Teledyne Wah Chang in a separate study\cite{19} suggest that material purity plays the stronger role in the residual resistivity ratio of Nb.

Due to the compelling data suggesting impurities are the primary cause (especially that proposed by [6]), suggests that the majority of the effect comes from non-superconducting impurities present in the film. Experimentation done to date has focused solely on the purity of the deposited film as a function of the residual gases present in the vacuum system during deposition\cite{11} with no attention to the original purity of the source Nb material used for deposition.

1.3 Electrotransport Purification (Background)

Due to the lack of attention paid to source niobium purity and the compelling evidence that film purity is the driving force behind residual resistance present in Nb/Cu thin films, the major thrust of this investigation will be to determine the effect of source niobium purity as well as the vacuum environment during deposition. The method planned to achieve ultrapurification of the niobium source material is a process called electrotransport (or electromigration) purification. Electrotransport purification is achieved by running a very high density DC current through the material to be purified under UHV conditions in order to cause the migration of solute atoms (impurities) present in the material toward the ends of the rods. The exact direction of the migration of impurities depends heavily on the material being purified, and can be either with\cite{20} or against\cite{21} the applied DC current. Figure 1.6 shows two different electrotransport purification assemblies. In both cases, special adaptors had to be made and attached to
each end of the specimen in order to establish a gradient across which impurities can migrate under the DC current while avoiding back-diffusion of impurities from the adaptors into the material being purified. These adaptors also serve the purpose of accommodating the thermal expansion of the sample and minimizing the temperature gradient at either end of the specimen, thus minimizing problems associated with this process\textsuperscript{[20]}.  

As seen in [7], when a sample of thorium was electrotransport purified, a two order of magnitude increase in the RRR value of the thorium sample was observed. In this study, as-received thorium with a measured RRR of 35 was electrotransport purified at progressively lower pressures, yielding a RRR levels approaching 2400. The primary residual gas in UHV is hydrogen. Figure 1.7 shows the results of this investigation, and demonstrates the effectiveness of this procedure under the vacuum conditions at which it is performed. The results of this and other studies\textsuperscript{[20,21]} provide no indication that a similar increase in performance should not be expected for niobium, and thus provide extremely compelling evidence for the use of this process to purify niobium samples for use in thin film deposition of Nb/Cu SRF cavities. The electrotransport properties of Nb are already well defined\textsuperscript{[21]} and make the electrotransport purification of niobium a relatively simple
The process providing one has the proper equipment. Although nitrogen is not a likely impurity issue, hydrogen, carbon and oxygen are, and perhaps other interstitials as well.

The purpose of this study was to electrotransport purify a niobium source specimen in UHV and to vapor deposit a Nb thin film on Si (100) and sapphire substrates under UHV conditions. The superconducting and material properties were measured and compared with thin films grown using as-received niobium.

Figure 1.7: Improvement of RRR for electrotransport-purified thorium\textsuperscript{[7]}
2. Theory

2.1 Electrotransport Purification (Theory)

As stated earlier, electrotransport purification is a process by which one is able to cause the migration of impurities present in a metal sample by passing a high current density DC current through the sample under UHV conditions. In order to predict how pure the sample can be made, several parameters must be known, including the mobility, \( U \) (expressed in units of \( \text{cm}^2/\text{V-sec} \)), of the interstitial impurities (solutes) and their diffusion coefficients, \( D \) (expressed in units of \( \text{cm}^2/\text{sec} \)), under the specific temperature and applied electric field, \( E \) (expressed in units of \( \text{V/cm} \)), at which the purification will take place\[^7\]. These constants can be found in the literature, or calculated experimentally using the method detailed in [21]. Having determined the values of \( U \) and \( D \), one can then calculate the ratio of the mean concentration, \( \frac{C_m}{C_0} \), for the solutes in the purer half of the rod at any time, \( t \), up to and including steady state, according to the relation:

\[
\frac{C_m(t)}{C_0} = 2 \left[ \frac{1 - e^{-S/2}}{1 - e^{-S}} - \sum_{n=1}^{m} C_n e^{-S/4} \sin \left( \frac{n\pi}{2} \right) e^{-\lambda n t} \right]
\]

(2.1)

where

\[
C_n = \frac{32n\pi S \left[ 1 - (-1)^n e^{S/2} \right]}{\left( S^2 + 4n^2\pi^2 \right)^2}
\]

\[
\lambda_n = \left( n^2\pi^2 + \frac{S^2}{4} \right) \frac{D}{l^2}
\]

\[
S = \frac{U}{D} El
\]
Here, \( n \) is the summation parameter in the infinite series and \( l \) is the length of the rod. These equations assume negligible impurity transport past the end of the rod and a length to diameter ratio such that the sample rod can be treated as one-dimensional. Calculating the values of \( \frac{C_m}{C_0} \) allow for an approximate determination of the time to steady-state concentration for each impurity of interest, yielding a good estimate of the time necessary to run the purification in order to achieve optimum results. For this study, electrotransport purified niobium was provided by the Ames Laboratory at Iowa State University. Conditions under which the purification took place were similar to those outlined in [21].

### 2.2 Physical Vapor Deposition

The films in this investigation were deposited using physical vapor deposition (PVD), or specifically electron beam evaporation. This method uses electron bombardment to heat the source material to its melting point (\( T_{m, Nb} = 2750K \)), creating a melt ball on the end of a target Nb rod from which evaporative deposition takes place on the substrate as a function of the vapor pressure of the material. The evaporative flux from the source can be calculated according to the equation:

\[
\nu_{evap} = \frac{C(p_v - p_0)}{\sqrt{2\pi mk_bT}} \tag{2.2}
\]

where \( p_v \) is the vapor pressure of the material being deposited, \( p_0 \) is the pressure above the surface (usually negligible under UHV conditions), \( m \) is the mass of the atom of the material being deposited, \( T \) is the temperature of the material (which for PVD will be the melting point of the material), and \( C \) is a constant that depends on the rotational degrees of freedom in the liquid and vapor states (which for an atomic source is approximately 1).
Plugging in the appropriate parameters for niobium and assuming $C=1$ and $p_0=0$, we find that $v_{evap} = 1.1 \times 10^{17}$ atoms/cm$^2$ s. To determine the flux experienced at the substrate, we can apply the principle of conservation of flux:

$$4\pi r_{mb}^2 v_{evap} = 4\pi r_{subs}^2 v_{subs}$$  \hspace{1cm} (2.3)

where $r_{mb}$ is the radius of the melt ball, $r_{subs}$ is the distance from the melt ball to the substrate, and $v_{subs}$ is the evaporative flux, or deposition rate, experienced at the substrate. Using the appropriate values, we find that for the experimental setup with $r_{subs} = 5$ cm, the theoretical deposition rate is $4.4 \times 10^{-2}$ monolayers/second, or 4.4 Å/minute. According to Mattox, however, the actual deposition rate may be anywhere from $1/3$ to $1/10$ of the value calculated using this method because of collisions in the vapor above the surface, surface contamination and other effects (i.e. $C\neq 1$, $p>0$)\textsuperscript{22}. 

---

\textsuperscript{22}
3. Experimental Design

3.1 Depositing Niobium Thin Films

Deposition of niobium thin films was conducted via physical vapor deposition (PVD) in a multifunctional electron and surface analysis system (MESAS), which consists of a main and introduction chamber (Figure 3.1a). Samples can be transferred via a magnetically-coupled linear motion transfer arm through an isolation valve that separates the two chambers. The main chamber contains a multi-sample carousel capable of angle-resolved Auger electron spectroscopy (ARAES), angle-resolved X-ray photoelectron spectroscopy (ARXPS), temperature desorption spectroscopy (TDS), electron energy loss spectroscopy (EELS), field emission energy distribution (FEED), depth profiling by Ar$^+$ sputtering and ultrahigh vacuum in the range of $\sim 10^{-11}$ torr. The introduction chamber has a base vacuum pressure of $\sim 10^{-9}–10^{-10}$ torr (depending on the...
pumping configuration), and houses a PVD deposition gun and a degassing filament that is also capable of glow discharge cleaning (GDC).

Due to the extremely slow deposition rate ($\nu \sim 0.1\text{nm/min}$), it was necessary to perform a full deposition in stages spaced out over a period of several days. Depositions were performed using a UHV PVD gun (Figure 3.1b, Figure 3.2). The source material used consisted of a ~1mm diameter niobium rod with a length of approximately 50mm. The source rod was bombarded with 11-12mA, 2kV electrons to form a liquid drop, or melt ball (from surface tension) on the end of the rod. The Si (100) substrate was oriented normal to the niobium rod axis at a distance of approximately 5cm. Niobium atoms evaporate to vacuum from the melt ball due to the vapor pressure ($p \approx 1.2 \times 10^{-3}\text{ torr}$)$^{[23]}$ at the melting point ($T_m \approx 2468^\circ\text{C}$)$^{[5]}$, and deposit on the substrate, providing a uniform
niobium coating. The uniformity of the coating is highest the further the gun is from the substrate, but with a concomitant decrease in deposition rate.

Figure 3.2: MDC physical vapor deposition gun (original configuration with solid tantalum shield). Inset is the evaporator head. The niobium rod (blue) is headed by electron bombardment from a tungsten filament.
3.1.1 PVD Gun Modification

Prior to niobium film deposition, a calibration deposition was performed using molybdenum to determine the impurity gas levels present in the system during deposition. A quadrupole mass spectrometer (SRS 100) was mounted on the introduction system to take measurements of the impurity gas partial pressures during the deposition. Successive comparisons of the vacuum background and the vacuum during deposition revealed within a dominant H₂ background, significant CO partial pressure present in the system. Significant levels of H₂O and CO₂ were also detected. Comparable CO levels were observed with the system in degas mode. As shown in Figure 3.3, the CO impurity was approximately 4% of the total pressure in the system, which for a high-purity experiment was an unacceptable level of contamination.

The most likely source of this gas impurity was from a higher pressure region (~15 times higher than the background pressure) located inside of the tantalum shield surrounding the source rod (shown in Figure 3.2) directly impinging on the thin film of Nb being deposited. It has been previously reported that CO and CO₂ are thermally and kinetically generated by adventitious surface carbon reacting with the surface oxide on the Ta shield in the reaction[24]: Ta₂O₅ + 5C → 2Ta + 5CO↑. It is expected that the Ta
shield gets sufficiently hot from the melt ball (T~2730K) that it radiatively heats up the surrounding stainless steel vacuum envelope to >400ºC so that it will also generate CO according to the reaction\(^\text{[25]}\): \(\text{Cr}_2\text{O}_3 + 3\text{C} \rightarrow 2\text{Cr} + 3\text{CO}↑\). This CO is simultaneously incident on the substrate and chemisorbs on the growing film at a rate that is sufficient to contaminate the Nb film – approximately \(4 \times 10^{14}\) atoms/cm\(^2\)-sec in the unmodified configuration (calculated using Equation 2.2). Using the values obtained from Equation 2.2, it was calculated that \(\frac{V_{\text{Nb}}}{V_{\text{CO}}} \approx 20\), meaning that during deposition, the CO deposition rate was only a factor of ~20 slower than the Nb deposition rate. Assuming a CO sticking coefficient of ~1, this means that the total impurity level of C and O could be as high as 10% of the total material deposited.

In order to reduce this background pressure, the Ta shield was modified from a solid structure to a grid (72% transmission) structure, shown in Figure 3.4. By changing to this configuration, an approximately 80-fold improvement in conductance through that region was achieved, which substantially lowered the overall CO partial pressure in the system.

![Figure 3.4: Modification of the tantalum shield from a solid configuration (a) to a grid configuration (b) to allow for better pumping of the higher pressure region formed inside the shield during deposition.](image-url)
3.1.2 Auger Electron Spectroscopy

Auger electron spectroscopy (AES) was one of several methods utilized to monitor thin film growth. AES is a surface analysis technique that uses a focused electron beam (diameter of beam ~75µm) of energy 2-50 kV to perform elemental analysis of the first 1-3 nm\textsuperscript{26} of a surface. The mechanism works as follows: an incident electron with sufficient energy strikes a core shell electron of an atom on the surface of the film, ejecting it from the atom and leaving behind a vacant site, or hole. An outer shell electron can then drop down into the hole left behind, releasing energy equal to the difference in orbital energies between the two electrons. This radiationless transition, in turn, can eject a second outer shell electron – called an Auger electron – that has a characteristic energy based on the atom from which it came. Figure 3.5 illustrates the Auger process.

Figure 3.5: Two depictions of the Auger process. (a) Shows the electron collision to eject a core level electron, followed by the simultaneous filling of the vacant site and ejection of the Auger electron (b) Spectroscopic notation for the same process.
MESAS uses a double pass cylindrical mirror analyzer (CMA) to collect and analyze emitted Auger electrons. The CMA contains both the electron beam source (coaxial gun) that is directed at the material to be analyzed as well as the detector for these electrons. The emitted Auger electrons are directed around the incident electron beam to an electron multiplier that serves as a detector located behind the source. Figure 3.6 shows a schematic of a double pass CMA similar to the one used in MESAS. In a double pass CMA, the electrons are directed in a figure eight pattern around and behind the detector rather than a simple ellipse. This is favorable because it eliminates background signal generated from electrons scattered from the walls around the electron gun during the first pass, giving a resolution \( \frac{\Delta E}{E} = 0.006 \). Detection limits in AES are governed by the signal to noise ratio as well as the elemental sensitivity, but generally are between 0.1-1% of a monolayer\(^{26} \). The Auger surveys used in this investigation were obtained using an electron energy, \( E_e = 3\,\text{kV} \) and an incident flux, \( I = 1\,\mu\text{A} \).
3.1.3 X-ray Photoelectron Spectroscopy

Another method used in this study to measure film purity is X-ray photoelectron spectroscopy (XPS). XPS in this investigation utilizes the x-rays given off from either a magnesium or an aluminum Kα x-ray source. The x-rays emitted from the Mg source used in this study strike the sample with energy, \( h\nu = 1253.6 \pm 0.7 \text{ eV}^{[26]} \) causing the ejection of a core shell electron. These emitted electrons have the same energy as the incident x-ray radiation; however, this energy is divided between the binding energy and kinetic energy of the ejected electron. If one then passes these emitted electrons through the aforementioned CMA that can reduce the electron kinetic energy to a known value.

![Diagram](image)

Figure 3.7: (a) Depiction of the XPS photoemission process. X-ray photons eject a core shell electron that is then slowed to a known kinetic energy to determine its binding energy for elemental analysis\(^{[26]}\) (b) Schematic of X-ray source head used to irradiate the sample surface.
(retarding field), it is then possible to determine the binding energy of the emitted electron and thus the atom from which the photoelectron came. Figure 3.7 illustrates the XPS photoemission process and shows a schematic of the x-ray source head used for sample irradiation. XPS is another surface sensitive process, with most of the signal obtained coming from the first ∼2-7nm\[^{26}\] of the sample surface, depending on the material being analyzed. Typical limits of detection for XPS experiments are approximately 0.1 atomic\%^{26}\].

3.1.4 Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy

Scanning electron microscopy (SEM) was used in this study to determine the surface morphology and thickness of the samples. SEM is used primarily as an imaging tool to see features too small to be observed via optical microscopy methods. The SEM used in this study was a Hitachi S-4700 High-Resolution Cold Cathode Field Emission SEM. Electron emission is obtained by applying a high voltage to an ultrasharp monocrystalline tungsten tip. At a high applied field (E > 1kV) electrons will tunnel out of the tip and into vacuum. The electron flux is then accelerated and reduced in size through a series of apertures running down the length of the column, focused and rastered through an objective lens containing deflection coils at the end of the column forming a beam with ~1nm diameter. Typical beam energies range from 1kV-30kV, depending on the sensitivity of the sample to high electric fields. An image is generated when secondary, or elastically scattered, electrons from the sample strike a scintillator, which creates photons that are then passed through a photomultiplier to generate an amplified signal that is then interpreted as an image. Different materials and morphological
structures have different secondary emission coefficients, thus providing surface contrast. Figure 3.8 is a schematic of the Hitachi S-4700 FESEM used in this study.\textsuperscript{[27]}

Figure 3.8: Hitachi S-4700 High-Resolution Cold Cathode FESEM (EDS assembly not pictured)\textsuperscript{[27]}
The spectroscopy used in this study for elemental analysis that is closely linked with SEM is energy dispersive x-ray spectroscopy (EDS or EDAX). EDS makes use of the inelastic interactions between the electron beam generated for SEM imaging and the sample. When the electron beam strikes the sample, some of the electrons are inelastically rather than elastically scattered, meaning that they transfer some of their energy to electrons in the sample when they collide. This energy transfer causes the emission of both x-rays and electrons (called backscattered electrons, BSE) in processes similar to XPS and AES. These emitted x-rays and BSE have energies that are dependent on the atom from which they came, and can thus be used for elemental analysis. In EDS, the emitted x-rays are used to get an idea of the local elemental composition of a sample. Compared to AES and XPS, EDS is much less surface sensitive – able to detect x-rays from approximately 1µm into the sample surface\[^{28}\]. This is due to the (usually) much higher energy of the electrons striking the sample surface. It is beneficial because it allows the user to obtain chemical information more representative of the bulk. The tradeoff to this surface sensitivity is decreased limits of detection, with 1.0 atomic% usually being the highest achievable sensitivity\[^{28}\]. This spectroscopy combined with XPS and AES gives a more complete assessment of the sample chemical composition.

### 3.1.5 Atomic Force Microscopy

Atomic force microscopy (AFM) was used in this study to determine film thickness for the thin film deposited from electrotransport-purified Nb in an effort to preserve the sapphire substrate on which it was grown. AFM is a form of scanning probe microscopy, where an ultrasharp tip attached to the end of an oscillating cantilever is
scanned across a sample surface in such a way as to gain topographical information about the sample. The AFM used for this study was a “Tapping Mode” AFM. In this method, the cantilever is oscillated at or near its resonance frequency (~20-100nm) and is allowed to lightly “tap” on the sample surface during scanning[29]. The motion of the cantilever is monitored by a split photodiode detector, which measures the deflection of laser light reflected off the back of the cantilever. Topographical information is achieved by maintaining a constant RMS of the oscillation signal detected by the split photodiode detector, a correction that varies with the height of features on the sample surface. Figure 3.9 is a schematic of the AFM apparatus used in this study. Tapping mode AFM is useful for film thickness determination in that it has a high lateral resolution (1–5nm)[29] and can therefore resolve a very sharp transition – i.e. the sharp change in height from the substrate to the top of the thin film caused by a scratch.

3.2 Residual Resistivity Ratio Measurement

The residual resistivity ratios used to judge the quality of the films deposited in this study were obtained via the four-point-probe method. A four-point probe consists of four spring-loaded probes arranged in a line similar to the schematic shown in Figure

Figure 3.9: Schematic of the “tapping mode” AFM system used to determine Nb-sapphire film thickness[29]
3.10. Probes A and B are connected to a constant current source, while a high-sensitivity voltmeter reads the voltage across probes C and D. The resistance of the thin film is the ratio of the measured voltage to the output current of the power supply. The four point probe used in this study is capable of being submerged in liquid He and thus the sample resistance can be measured at temperatures as low as ~4K. However, since the $T_c$ of Nb is 9.3K and there is no resistance in the superconductive state, the low temperature resistance for RRR determination was measured at 10K.

Figure 3.10: Schematic of a four-point probe setup for niobium thin film RRR measurement. The envelope surrounding the sample allows for temperature control from $T=300K-4.2K$. 
4. Results and Discussion

4.1 PVD Gun Modification

A significant carbon monoxide partial pressure generated in the system during deposition necessitated the modification of the tantalum shield surrounding the source niobium rod from a solid to a grid structure as shown in Figure 3.4. The PVD gun had previously been moved closer to the sample – from a source-to-substrate distance of 12.5cm to a distance of 5cm – in order to increase the Nb deposition rate. However, this change most likely had the unexpected side effect of increasing the CO flux experienced by the substrate during deposition. To further characterize the time-dependent effects of CO exposure on impurities present in a sample, a polycrystalline molybdenum substrate was sputter-cleaned in the analysis chamber to obtain a baseline AES spectrum. This sample was then exposed to the degas mode (no deposition) of the PVD gun for successively longer periods of time, with AES surveys taken at each time interval (\(E_e=3kV\) and incident flux, \(I = 1\mu A\)). The ratio of carbon and oxygen peak intensities to the molybdenum peak intensity at each interval was then measured in order to monitor the change in impurity levels with time. As shown in Figure 4.1, impurity levels on the surface of the substrate increased very rapidly (\(p\approx 1x10^{-7}\) torr with Evap 100 filament at 10mA) for approximately 10 minutes.
before reaching an asymptotic limit, suggesting that the surface adsorption sites were eventually saturated. The initial slope of this curve will most likely be even steeper for niobium due to the fact that it has a much higher sticking coefficient for carbon and oxygen than does molybdenum – $0.9^{[30]}$ vs. $0.2^{[31]}$. Furthermore, Nb is an excellent getter for hydrogen, but unfortunately AES and XPS cannot detect it. This result is important in that it demonstrates that even a short period of exposure to the CO contamination present in the system results in significant adsorption of carbon and oxygen onto the surface of a sample. This is also important because the adsorption will be continuous rather than asymptotic during a deposition, meaning that a large, continuous contamination will be incorporated into the film throughout the deposition. Because of this fact, modifying the tantalum shield geometry was necessary to minimize this effect.

In order to determine the improvement in quality of the films achieved by modifying the Ta shield, a Nb film was deposited for 60 minutes before the grid structure was put in place and compared to an equivalent deposition after the shield was modified to the grid structure. After deposition, the samples were transferred into the analysis chamber and AES surveys were taken ($E_e = 3\text{kV}$ and incident flux, $I = 1\mu\text{A}$). The results are shown in Figures 4.2a and b.
Figure 4.2: Nb film AES spectra collected (a) before and (b) after Ta shield modification. Both the C and O peaks decreased significantly, confirming a decrease in the CO partial pressure during deposition mode.
Note in Figure 4.2a the very high oxygen and carbon signals in the film even though the CO partial pressure within the intro chamber was only ~$1 \times 10^{-8}$ torr during deposition. This supports the claim that there is a region of higher pressure inside of the Ta shield because the CO partial pressure is not high enough to cause this level of contamination without some additional flux of CO towards the substrate during deposition. As seen in Figure 4.2b, with the grid structure in place a marked decrease in the concentration of C and O took place. In fact, comparison of the ratios of the C(270eV)/Nb(167eV) and O(508eV)/Nb(167eV) peak intensities before and after the modification show that the C concentration decreased by a factor of ~6.5 and the O concentration decreased by a factor of ~4.4. This change shows that a decrease in the CO flux towards the substrate was achieved, meaning that the conductance improvement, coupled with the gettering effect caused by Nb deposition on the chamber walls, successfully lowered the CO partial pressure inside and outside the Ta shield. However, the fact that AES is able to detect these impurities at all means that the level of contamination caused by the CO impurity is too large and will obscure the gain in thin film purity between the as-received and electrotransport-purified Nb source rods. This is due to the fact that the limits of detection of AES are at best ~1.0 atomic%, whereas the difference in purity between the as-received and electrotransport-purified rods is less than 1 atomic%. This means that if an impurity of greater than 1 atomic% is inherently deposited onto any film grown by this method, any gain in thin film purity between the two source rods may be effectively lost.
4.2 Deposition Rate and Film Thickness

4.2.1 AES Deposition Rate Determination

Using AES, it is possible to calculate an estimate of the Nb deposition rate for this method. The film thickness can be measured as a function of the drop-off in intensity of the signal from the Si substrate\(^{32}\) (in the case of the film grown from as-received Nb) as given by the equation:

\[
x = -\mu_0 \ln \left( \frac{I_{Si}}{I_{0, Si}} \right)
\]  

(4.1)

where \(x\) is the film thickness, \(\mu_0\) is the inelastic mean free path of Nb, \(I_{0, Si}\) is the silicon peak intensity of the bare Si substrate and \(I_{Si}\) is the silicon peak intensity after niobium deposition for a fixed time. Figure 4.3a and b show the spectra used for this calculation.
Figure 4.3: AES surveys used to determine deposition rate. (a) is the baseline spectrum from the bare Si substrate and (b) is the spectrum obtained from a Nb film deposited for 45 minutes.
It was found that the film thickness after 45 minutes of deposition was 1.5nm, giving a deposition rate of \( \sim 0.3\text{Å/min} \). This value, however, was for an incident \( \text{e}^-\) current of 11mA during deposition. Later current levels (\( \sim 12\text{mA} \)) most likely increased the size and average temperature of the melt ball, and therefore the deposition rate. This is possible because the smaller melt ball on the end of the rod was the result of higher thermal conduction down the length of the rod (pictured in Figure 4.4). At higher input power (\( P \sim 24\text{W} \)) the melt ball became larger, increasing the surface area at \( T_m \) and therefore the local surface temperature of the melt (\( T_s > T_m \)).

4.2.2 SEM Determination of Film Thickness

To determine the exact thickness of the deposited films, SEM images were taken of cross-sections. The film grown from the as-received niobium rod was deposited for a
total of 49 hours, or 2940 minutes with an incident e− current of 12mA. As shown in the SEM image in Figure 4.5, the thickness of the as-received film was approximately 280nm. This corresponds to a deposition rate of approximately 1.0Å/min, while the theoretically calculated deposition rate was approximately 4 times faster than the actual rate. The difference between the theoretical calculation and the actual rate falls well within the range predicted by Mattox and is therefore not an unexpected result. On the other hand, the difference between the actual rate and the rate calculated using Auger is most likely caused by three factors. First is the fact that the potential exists for measurement errors of up to 30% for thinner films (<20Å) due to Kikuchi and backscattering effects\cite{32}. The second reason is that film thickness is most likely not uniform across the entire sample substrate due to the fact that the substrate is not heated during deposition. This means that when incident niobium atoms strike the surface they are essentially fixed at that location (localized adsorption), leading to uneven nucleation and growth on the sample. Because of this uneven surface morphology, a local measurement by Auger could report a lower (or potentially higher) value for the film thickness, leading to error in the determination of deposition rate. SEM images taken of

![SEM image](image.png)

**Figure 4.6**: Side-by-side comparison of SEM cross-section of Nb thin film with Figure 1.4\cite{5}. Open boundaries and voids are not clearly visible; however, the obvious grain boundary structure is almost identical to that pictured in the conceptual drawing.
the samples support this theory, as significant variation in the height of the film across the surface, as well as a columnar structure similar to that illustrated in Figure 1.4 is observed. Figure 4.6 shows a side-by-side comparison of the columnar grain growth observed with that pictured in Figure 1.4. Other relevant features of the film are highlighted in Figure 4.7. The third factor is that the incident energy could affect the size and average temperature of the melt ball. The surface temperature on the melt ball could in fact be higher than $T_m$. Since the deposition rate is directly proportional to the vapor pressure, which is exponential with temperature, an increase of 100K can cause an increase of greater than a factor of two.

![Figure 4.7: Surface and structure morphology of the film deposited 49h from as-received Nb. Clearly visible are a columnar grain structure and an uneven surface height.](image)

The poor film structure exhibited by these films is not fully understood, but is not of great concern because it is a problem that can easily be solved by heating the substrate during deposition. This increases the surface adatom mobility, most likely allowing for more uniform nucleation and growth across the entire surface of the sample. In fact, this
effect was observed for even moderate substrate heating (T=300ºC) during the deposition of electrotransport-purified Nb on to sapphire. Figure 4.8 is an SEM image of the surface of the film. Even up to 100,000 times magnification with a piece of dust present on the film used as a reference for contrast, no noticeable imperfections are visible on the sample surface. Since the main thrust of this investigation is film purity rather than structure, this issue will not be treated further, but would be an interesting avenue of exploration in a future study. For example the work of Wolf et al. in depositing Nb on single crystal Al₂O₃ substrates showed that epitaxial Nb films can be grown if the substrate temperature is maintained at 700ºC or higher, with the best results achieved at 850ºC on Al₂O₃(0001)\textsuperscript{18}.

4.2.3 AFM Determination of Thin Film Thickness

SEM determination of thin film thickness required cleaving of the Si(100) substrate along crystallographic boundaries in order to achieve a clean cross-section of the thin film. However, due to the lack of crystallographic planes (and concurrent resistance to fracture) of the sapphire substrate used in the Nb thin film deposition from the electrotransport-purified source, a non-destructive method to determine thin film thickness, such as AFM, was needed. In order to obtain an estimate of the thin film
Figure 4.9: AFM thin film thickness determination. (a) is a 3-D representation of the topography across a scratch made in the sample. (b) is a section analysis across the scratch from which the thin film thickness was determined.
thickness, a scratch was made across the thin film surface. To ensure the substrate was not scratched along with the thin film (which would skew the ensuring thickness measurement), a used STM tip made of PtIr was used to make the scratch. PtIr has a hardness greater than that of Nb, but less than that of Al₂O₃, meaning that only the Nb would be affected by scratching of the surface. Figure 4.9 is a summary of the data obtained from AFM.

The 3-D projection of the topography across the scratch in Figure 4.9a shows both that only the Nb thin film was scratched by the STM tip and that the tip was sharp enough to make a scratch with walls that are approximately perpendicular to the substrate surface. The section analysis in Figure 4.9b supports this observation, with a 2D projection of the surface topography showing the sides of the scratch to be almost perpendicular to the substrate surface. This favorable topography allows for a reasonably accurate determination of the overall thin film thickness from AFM. A second survey was taken across another scratch made across the sample surface, which yielded a similar result to that shown in Figure 4.9, and from this result it was concluded that the Nb thin film thickness was ~25nm. Assuming a similar deposition rate to that calculated for the as-received thin film, this value is approximately half the thickness expected for this film. This discrepancy is most likely due to fluctuations in the temperature of the melt ball as outlined earlier. Unfortunately, no information could be obtained about the grain structure of the thin film; however, the extremely flat topography of the film to either side of the scratch shown in Figure 4.9a supports the observations using SEM in Figure 4.8. These two pieces of data suggest that columnar grain growth did not take place on this film as a result of substrate heating during deposition.
4.3 Thin Film Purity

4.3.1 Energy Dispersive X-ray Spectroscopy

While imaging using SEM, EDS spectra were taken for the two Nb films grown to gain chemical data on the bulk elemental concentrations present in the samples. Figure 4.10 shows the results of the EDS surveys for the films deposited from the as-received and electrotransport purified Nb source rods.
Figure 4.10: EDS surveys of Nb thin films grown (a) on Si(100) from as-received Nb (99.9% pure) and (b) on Al₂O₃ using electrotransport purified Nb
As can be seen from these spectra, the limits of detection of EDS are too high to see anything more than large Si or Al and O peaks from the substrates and much smaller Nb peaks from the thin film. Attempts to perform EDS at an angle such that the e⁻ beam would pass only through the Nb thin film were unsuccessful, returning the same spectra as shown in Figure 4.10. This result suggests that EDS is not sensitive enough to detect impurities on the order of what is present in the thin films deposited for this study.

4.3.2 Auger Electron Spectroscopy

In order to gain a more accurate picture of the impurities present in the thin films, AES surveys were taken of the two Nb samples. Although Figure 4.2b was taken from a separate film deposited for 60min, it is sufficiently representative of any film deposited from the as-received Nb rod assuming that the Nb and CO incident flux is essentially constant between depositions – which it is. Therefore Figure 4.2b is used here as

![AES Survey: Nb Thin Film on Al2O3 Deposited 7h from Electrotransport Purified Nb Source](image)

Figure 4.11: AES spectrum of Nb thin film deposited for 7 hours on an Al₂O₃ substrate using the electrotransport-purified source rod. Clearly visible are significant Cl and O impurities.
representative of the impurities present in the film deposited for 49h from the as-received Nb rod. Figure 4.11 is an AES survey taken of the film deposited from the electrotransport purified source rod.

As seen from Figure 4.11, there is a significant chlorine impurity present on the film. This is most likely because the film was deposited using the impure end of the electrotransport-purified rod (the end to which all the solute impurities migrated to during the purification process). Furthermore, it is known that Ames-Iowa State used perchloric acid to clean the electrotransport purified Nb, which may be the source of this contaminant. A guide mark indicating which end of the rod was the impure end was lost during the machining process to make the rod thin enough to fit into the PVD gun. Because of this it was unknown which end was the correct one, which most likely led to the rod being inserted backwards and deposition proceeding using the contaminated end. Also found in this spectrum is a large oxygen peak; however, this is due to the fact that the sample was left in the introduction chamber for several days, which at the baseline pressure of the introduction chamber was long enough for the thin film to become completely coated by oxygen-bearing species present in the system. Unfortunately due to time constraints there was not enough time to deposit a film using the pure end of the rod, meaning that a RRR comparison with the film deposited from the as-received Nb will be meaningless. However, the topography data obtained from SEM is no less meaningful and is still indicative of how the deposition is expected to behave at elevated substrate temperatures.
4.3.3 X-ray Photoelectron Spectroscopy

XPS was utilized in order to gain a more complete picture of the impurities present in the thin films. An XPS spectrum was obtained of the thin film grown from the as-received Nb source, but not of the film grown from the electrotransport purified source. This was due to the heightened impurity level in the film from having been deposited using the wrong end of the rod. It was deemed that the sample could not be considered representative of a thin film deposited from an ultrapure source, and that it was therefore unnecessary to obtain more spectroscopic information from the film. Figure 4.12 shows the XPS spectrum of the thin film grown from the as-received Nb source.

![XPS Spectrum](image)

Figure 4.12: XPS spectrum of the thin film grown from the as-received Nb source rod.

Clearly visible are several Nb peaks corresponding to electrons from the various orbitals that can be stimulated by the energy of the incident X-ray radiation. Also visible are peaks coming from the carbon and oxygen deposited from the incident CO flux, supporting what was observed using AES.
4.4 Residual Resistivity Ratio

Residual resistivity ratios were determined using the four-point-probe method for the two films deposited as well as on the two source Nb rods. The data in Figure 4.13 was provided as a professional courtesy by Dr. Thomas Ambrose of Seagate Technology LLC, and showed that thin films deposited using magnetron sputtering of a high purity Nb target exhibit a poor RRR value of approximately 5.1\textsuperscript{[33]}. This data was encouraging in that it demonstrated that films deposited using this method – where the substrate is cold and significant amounts of the carrier gas (Ar) and the accompanying gas impurities used to sputter the source material are included in the deposited film – produce films of high disorder and low superconductive quality. Dr. Ambrose, who is an internationally recognized expert in thin film deposition, reviewed the MESA system and commented that the electron beam PVD method conducted in ultrahigh vacuum is the “best approach”\textsuperscript{[33]}. Since there is no carrier gas and there is a significantly lower level of impurity inherent to the method, this approach should produce films of superior superconductive quality. This, of course, is still contingent on the deposition rate, the purity of the Nb source and the relative CO contamination flux.

Figure 4.13: Resistance vs. temperature plot for a 100nm Nb thin film deposited onto a SiO\textsubscript{2} coated Si substrate with a 20Å Ta barrier layer via magnetron sputtering. This curve corresponds to a RRR of 5.1\textsuperscript{[33]}. 
Jefferson Lab was in the process of developing a good four-point-probe apparatus that could be exposed to the liquid He system and provide information about the resistances at 10K versus 300K. It is unclear whether this new apparatus had probes that would not make good contact with the thin films, or whether a problem existed with the apparatus itself. Regardless, the unforeseen problems with the deposition using the electrotransport purified source rod rendered any comparison between the two thin films meaningless. However, it was possible to obtain a partial plot of the resistance as a function of temperature using an electrotransport purified Nb slab obtained from Ames Laboratory at Iowa State University. Figure 4.14 shows the partial curve that was obtained.

![Residual Resistivity Curve for Electrotransport-Purified Nb Slab](image)

Figure 4.11: Residual resistivity curve obtained from electrotransport purified slab. The curve corresponds to RRR = 5.8 for 77K versus 300K.

Extrapolating the data linearly – which is a fairly accurate approximation above liquid nitrogen temperatures – yields a RRR = 5.8 for the ratio of the resistances at 77K versus 300K. Ames Laboratory determined a RRR = 5.7 (at the same temperatures as...
above) after electrotransport purification\textsuperscript{[34]}, which is almost identical to the value calculated from this plot. Unfortunately the curve behaves non-linearly below liquid nitrogen temperatures, and therefore further extrapolation from this curve is not possible. Ames Laboratory did not supply RRR for this material at 10K versus 300K; however, they did calculate RRR at these temperatures for electrotransport purified vanadium and tantalum, which are in the same group as Nb. The values they obtained were 2300 and 1800 for V and Ta, respectively, which suggests that the RRR for the Nb sample would be expected to fall in between those values. An estimate at the mid point would be approximately RRR=$2050\textsuperscript{[34]}$. 
5. Conclusions and Further Work

Niobium thin films were deposited from both as-received (99.9% purity) and electrotransport purified Nb source rods, and characterized using several surface analysis methods. A significant CO partial pressure generated in the system during Nb deposition was detected early in the experiment. This resulted in a large carbon and oxygen impurity level in the thin films to be studied and severely hampered the ability to conduct a viable comparison between the properties of films deposited from two sources with differing purities. This problem led to the movement of the PVD gun closer to the sample substrate and the modification of the geometry of the tantalum shield surrounding the PVD apparatus from a solid to a grid structure. The former increased the deposition rate and the latter allowed better pumping of the CO. The AES spectra taken before and after this modification showed a substantial decrease in the level of C and O present on the films; however the contamination from the background was still too large for the gain in purity between the as-received and electrotransport-purified sources to be significant. The C and O adsorbed and incorporated into the Nb during deposition could still be as high as 3%.

This work indicates that the impurity level incorporated into the thin films is an issue of related rates. That is, in order to reduce the carbon and oxygen impurities being deposited onto the thin films to acceptable levels, a method must be devised to increase the niobium deposition rate to a level substantially higher than the rate that carbon monoxide is deposited. For example, using Equation 2.1 it is possible to calculate the partial pressure of CO necessary to achieve an overall C and O impurity incorporation of $10^{-6}$ (1ppm) with respect to Nb according to the relation:
Using the theoretical Nb deposition rate calculated in Section 2.2, to achieve a ratio of \( \frac{v_{Nb}}{v_{CO}} = 10^6 \), a CO partial pressure of \( \sim 1.4 \times 10^{-10} \) torr is required, which for an electron beam evaporative deposition process is extremely difficult. However, increasing the Nb deposition rate by a factor of 100 lets the maximum allowed CO partial pressure to increase to \( \sim 1.4 \times 10^{-8} \) torr, which was the CO partial pressure present in the system before modification of the Ta shield.

Indeed, the temperatures involved with evaporative deposition of Nb are high enough (T > 2700K) that there will undoubtedly be enough radiative heating of the surrounding components to cause the reactions of adventitious carbon with the surface oxide of vicinal metal (e.g. the Ta shield and stainless steel sleeve) to form CO. This means that a CO flux towards the substrate will almost always be present at some level during an evaporative deposition process. This must be managed by good UHV design to keep the background at \( 1 \times 10^{-8} \) torr or better. However, increasing the Nb deposition rate with respect to the CO deposition rate can be accomplished by e− beam evaporation techniques as well. Simultaneously, reducing the pressure of these thermally generated gases will minimize the contamination rate. Knudsen cells, such as the one pictured in Figure 5.1, allows the Nb to be superheated above its melting point during deposition. This substantially increases the vapor pressure of the Nb and thus increases the deposition rate. An increase in the temperature of the melt to 3000ºC will provide the vapor pressure needed to gain a factor or >100 in deposition rate. Assuming the CO flux
is managed by good system design (1x10^{-8} torr or less), the amount of carbon and oxygen incorporated into the film per monolayer of Nb will be less that a ppm. It should also be noted that H\textsubscript{2}, CO\textsubscript{2} and H\textsubscript{2}O are a concern. If the substrate is heated, H\textsubscript{2} and H\textsubscript{2}O should not be a problem, but the same concerns for CO are also applicable to CO\textsubscript{2}. Further experiments would be needed to confirm this hypothesis, but it is likely that this approach is a viable solution to the problem.

Data collected during the RRR experiment strongly support the original premise of this study. For instance, the data supplied by Dr. Thomas Ambrose shows that magnetron sputtering of high purity Nb produces thin films with a very high defect density and correspondingly poor RRR values (RRR~5.1). Additionally, the data from Wolf et al. indicates that purity is the dominant issue because the highest RRR value achieved by the study was only 87 for a single crystal Nb thin film\textsuperscript{[18]}. Finally, the 99.9999\% pure polycrystalline Nb sample provided by Teledyne Wah Chang had a RRR = 452\textsuperscript{[19]}, again strongly indicating the dominant role of purity.

Clearly, there is an intertwined role of thin film purity and defect density on the superconductive properties of Nb thin films, but the extent of the effect that either purity or defect density has on RRR is unknown. Since there seem to be two competing

Figure 5.1: Schematic of a simple Knudsen cell
processes influencing superconductive quality, it is very likely that were one to determine RRR versus either defect density or impurity concentration, a crossover point exists. Figure 5.2 is a speculative representation of such a curve. Based on the almost exponential relationship between purity and RRR obtained from [7], it is believed that impurity concentration will become the dominant effect influencing RRR as both defect density and impurity concentration decrease. A detailed study investigating the coupled effects of defect density and purity would certainly be a worthwhile endeavor in the hopes of better understanding what factors must be taken into consideration when depositing thin films for use in linear accelerator cavities.

Figure 5.2: Speculative curve representing the competing effects of impurity concentration and defect density on the RRR of deposited Nb thin films
6. **Acknowledgements**

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7. References


