Optical Properties of Ultra-Thin Niobium Nitride Films for Single Photon Detectors

by

Lucy Elizabeth Archer

Submitted to the Department of Physics
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Abstract

In this thesis I made a study of the properties of reactively sputtered ultra-thin films of niobium nitride (NbN) and niobium titanium nitride (NbTiN). Using Variable Angle Spectral Ellipsometry (VASE), I found that the optical properties of NbN films appear to have a critical thickness above which the optical parameters stabilize. I also found that the deposition process has better stability over time for thicker films than for thinner ones; that is, when films are deposited weeks apart, the thinner films show more variation in thickness and optical properties than do the thicker films. The data also suggest that the crystallinity of the substrate upon which the NbN is deposited has a significant effect on the optical parameters. The set of films deposited for the optical study was also tested against a universal scaling law for thin film superconductors, which seems to support the existence of the critical thickness, below which the properties change significantly and do not conform to the power law scaling that holds for thicker films. Finally, I explored recipes for depositing NbTiN with our sputtering system, in the hope of creating films that have better properties than NbN to be used in device manufacturing. I was able to create films with the same properties as our current NbN films with minimal optimization, and further work in this area should result in NbTiN films that are better than our NbN films.

Thesis Supervisor: Karl K. Berggren
Title: Professor

Thesis Supervisor: Vladan Vuletic
Title: Professor
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Chapter 1

Introduction

Superconducting nanowire single photon detectors (SNSPDs) are used in a number of fields, including characterization of quantum emitters [41], integrated circuit testing [38], light detection and ranging (LIDAR) [28], and quantum key distribution [36]. Their fast reset time, small timing jitter, high detection efficiency, and the wide range of wavelengths over which they can operate make them a critical component in many current experiments. The most frequently used material for SNSPDs is niobium nitride (NbN), which is generally deposited by reactive sputtering as an ultra-thin (~ 5 nm) film. NbN is an excellent material for use in SNSPDs due to its high superconducting temperature, fast cooling time, and the ease with which the devices can be fabricated and operated [11]. A high superconducting temperature allows operation of the devices at liquid helium temperatures, eliminating the need for expensive sub-4 K cryogenic systems. The fast cooling time means a fast reset time between triggering events. NbN SNSPDs can be deposited, patterned, and operated with instruments readily available to our, and many other, group(s), so that specialty equipment is not required for device fabrication, nor does any step have to be done by an external company or facility.

As the primary material used for SNSPD fabrication, NbN has been used since the devices were first demonstrated in 2000 and has been generally quite successful. Other materials, such as tungsten silicide (WSi) and niobium titanium nitride (NbTiN) have recently come into use for SNSPD fabrication. The homogeneously disordered
structure of WSi makes it more robust against structural defects than NbN, and allows more degrees of freedom for optimizing the absorption and optical coupling of the detectors [27]. The downside to WSi is its low superconducting critical temperature, which requires operating temperatures below 2K. NbTiN is very similar to NbN in its crystal structure and properties, but has been shown to have higher critical temperature and lower sheet resistance, as well as being less sensitive to small changes in deposition conditions. Though fabricating devices out of WSi requires gaining access to cryogenic systems that are expensive to acquire and operate, making devices out of NbTiN would require minimal changes to the rest of the fabrication process and could result in improved performance and device yield.

This thesis presents various studies done in the interest of improving the properties of the Quantum Nanostructures and Nanodevices (QNN) group’s SNSPDs. Our group has done relatively more work in optimizing detector design but has done less work on the materials used for the device itself; however, performance metrics such as detection efficiency are now at values where single percentage points are important, and so we are now investigating any possibility of gains through material optimization. This work explores the possibility of optimizing the optical properties of the NbN used to make detectors in order to improve device efficiency, examines a scaling law that could improve our understanding of how the devices trigger and thus how to improve their efficiency, and investigates the possibility of making NbTiN to be used for detector fabrication within the QNN group, as NbTiN generally has more favorable properties than NbN and could potentially produce higher quality devices.

Chapter 2 introduces SNSPDs, explains how they function, and explores possibilities for improving their performance. Through a discussion of the device tradespace—the trade-offs in performance according to various metrics—we conclude that the development of ideal nanowire materials and cavity systems for improving absorption are of immediate interest for improving device performance.

Chapter 3 presents a study of the optical properties of ultra-thin NbN films, with the ultimate goal of better understanding how the material behaves optically in order to improve SNSPD performance. Less work has been done in the literature on the
optical properties of NbN than on other properties, and in particular we were unable to find any information pertaining to NbN films deposited on amorphous substrates, like the SiO$_2$ we currently use for fabricating devices. We were rather surprised to find that there is a critical thickness at which optical properties stabilize, and that there appears to be a significant difference in optical properties for NbN deposited on crystalline and amorphous substrates.

Chapter 4 discusses the films deposited for chapter 3 in the context of a scaling law for thin film superconductors that was published by our group in 2014. Ivry et al. [20] extracted data from dozens of papers reporting the superconducting properties of thin films and found that critical temperature, thickness, and sheet resistance can be linked by a power law. The set of films studied in chapter 3 is the first time our group has deposited a series of different thickness films in a short time period, so it was interesting to see how they fit the scaling law. All films thicker than the critical thickness for optical parameters follow the scaling law, but the thinnest films deviate from the fit.

Chapter 5 reports on an exploration of the possibility of making NbTiN films with our deposition system. NbTiN has been reported to have better properties for SNSPDs than NbN does in terms of superconductivity, electrical properties, and deposition process stability and would be an excellent choice for device fabrication. We were able to find a film recipe that produces NbTiN films with properties identical to our best NbN films with only a few iterations, and there is still space to optimize the film properties. I am confident that it will be possible to produce thin NbTiN films that outperform NbN films.

Chapter 6 discusses the importance and usefulness of these results as well as questions that have been uncovered in the course of my research.
Chapter 2

Superconducting Nanowire Single Photon Detectors

A primary research area in the Berggren group is the fabrication and optimization of Superconducting Nanowire Single Photon Detectors (SNSPDs) [18, 29, 31]. When first demonstrated, SNSPDs were a welcome supplement to the photon counters that were available for the visible and near-infrared. Vacuum photomultipliers are slower and bulkier than is desirable, and have low quantum efficiency at longer wavelengths [10]; silicon photodiodes are limited to wavelengths shorter than 1 μm due to the silicon bandgap [15]; single-photon avalanche photodiodes exhibit low detection rates due to their complicated readout schemes [10]. There was a great need for near-infrared single-photon detectors for use in quantum communications and quantum computation, and the SNSPD fit these requirements perfectly.

SNSPDs were first demonstrated by Gol’tsman et al. in 2000 [10]. Their first detector was a single NbN nanowire that was approximately 10 nm thick and 200 nm wide, attached to the end of a 50 Ω transmission line, biased with a current close to the current at which the nanowire would switch from the superconducting state to the normal state; this current at which the device switches is the critical current, $I_c$. Their understanding of the operating principles of the device were that the absorption of a photon by the nanowire generates a resistive hot spot that effectively lowers the nanowire width at that location, causing the current density to exceed $I_c$, so that the
resistive spot spreads to cover the width of the wire through Joule heating; recent work has improved on this hotspot model, though in these new models the absorbed photon still leads to current redistribution, Joule heating, and a fully resistive region [6]. Once the wire is fully blocked by a normal region, current is diverted to the 50 Ω transmission line, allowing the heat in the wire to dissipate into the substrate, thus restoring the superconducting state and resetting the detector. Gol’tsman et al. also demonstrated the use of a meandered nanowire to absorb the photons, which provides coverage of a larger area in which photons could potentially be absorbed; the meander geometry is now the standard SNSPD configuration, as shown in figure 2-1.

Figure 2-1: An SEM image of patterned resist for a device before etching, provided by Karl Berggren. The (false colored) blue meandering wire in the center of the image is the detector; the blocks the nanowire is connected to are gold electrodes; the features at the top and bottom are for proximity effect correction for the electrodes. This particular device is 3 μm by 3 μm, with 90 nm wide nanowires and with the inner corners of the meander rounded for optimal current flow, to avoid the issues shown in figure 2-2. Our devices are generally made on 4 nm thick NbN films and have approximately 100 nm wide wires.
Beyond being able to detect wavelengths longer than 1 μm, SNSPDs also show high performance in other areas critical to many applications. Key parameters include timing jitter, the timing uncertainty between the arrival of a photon and the generation of the SNSPD output pulse; dark counts, the number of false detection events; maximum detection rate, or how quickly single photons can be counted, which is related to the reset time of the detector; bandwidth, the range of wavelengths detectable by a single detector; and efficiency, the probability that an output signal is generated when a photon is incident on the detector. Table 2.1 summarizes these parameters, and mentions the current state-of-the-art value that has been achieved.

<table>
<thead>
<tr>
<th>Key Metric</th>
<th>State of the Art</th>
<th>Material</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Timing Jitter</td>
<td>18 ps</td>
<td>NbN on MgO</td>
<td>L. You et al. [37]</td>
</tr>
<tr>
<td>Dark Counts</td>
<td>10⁻⁴ cps</td>
<td>NbN on SiO₂</td>
<td>H. Shibata et al. [34]</td>
</tr>
<tr>
<td>Data Rate</td>
<td>1.25 Gbit/s</td>
<td>NbN</td>
<td>E. Dauler et al. [4]</td>
</tr>
<tr>
<td>Bandwidth</td>
<td>350 nm to 10 μm</td>
<td>NbN on sapphire</td>
<td>F. Marsili et al. [26]</td>
</tr>
<tr>
<td>Efficiency</td>
<td>93%</td>
<td>WSi</td>
<td>F. Marsili et al. [27]</td>
</tr>
</tbody>
</table>

Table 2.1: Summary of key metrics for SNSPD performance and the current state-of-the-art.

2.1 Device performance tradespace

Despite their excellence, the benchmark results listed in table 2.1 come with caveats, primarily that the numbers achieved generally require a compromise in other areas of detection. For instance, the SNSPD reported by Marsili et al. with 93% system efficiency has a dark count rate of 1 cps, 150 ps timing jitter, and a 40 ns reset time, corresponding to a detection rate of 25 MHz. They also claim detection efficiency over 90% only in the wavelength range of 1,520–1,610 nm, due to the optical properties of the stack they used to improve absorption. The 10⁻⁴ cps dark count rate achieved by Shibata et al. comes along with a detection efficiency of only 2.3%, despite their use of a 260 nm thick SiO₂ cavity to improve absorption, which is of a length that our modeling indicates should result in maximal absorption.

Though a full analysis of the tradespace of SNSPD parameters has not been done,
there are certain tradeoffs that are evident from an understanding of how the devices function. Increasing the bias current will increase the detection efficiency, for reasons described in the following section, but this increase in bias current will also result in an increase in dark counts, since decreasing the photon energy needed to trigger the device will also lower the amount of thermal fluctuation the device can handle without triggering. Adding an optical cavity improves device efficiency but at the cost of bandwidth, since the cavity only concentrates certain wavelengths of light. Reset time, which is related to the maximum data rate, is limited by the kinetic inductance of the device; though the obvious solution is to minimize kinetic inductance, there is also a minimum inductance required to keep the device from latching, or being unable to reset after being triggered. Jitter will also affect the maximum data rate, though as it is orders of magnitude smaller than the current best reset time it is not a significant factor at this time.

Other tradeoffs have been discovered through testing devices. The existence of constrictions in devices is possibly a result of nonuniformities in the films used to fabricate devices, and is an impediment both to improved functioning of individual devices and to the reliable fabrication of uniform devices. Timing jitter seems to be related to the location at which a photon hits a device, so larger devices will have better coupling efficiency but larger timing jitter. Shibata et al. have made measurements indicating that the timing jitter decreases with increasing bias current, which is currently unexplained but may lead to better understanding of the origin of timing jitter. Ivry et al. [20] reported an empirical scaling law that relates sheet resistance, critical temperature, and film thickness, which could be useful both in evaluating film properties and in leading work to develop better films for devices.

Of course, there are many different applications for SNSPDs, each with their own requirements. In many cases the tradeoffs are not a huge sacrifice, and it is possible to optimize a detector for the required application. For instance, quantum communications require high coupling efficiency, which correlates to low bandwidth; in this case having low bandwidth is not an issue, as the system operates at a specific wavelength and thus only a small range of wavelengths must be detected. Also, as
each parameter improves, its ‘bad’ value will also improve, so that generally SNSPD performance will improve across the board. That said, a better understanding of how the performance metrics influence each other would be beneficial to our understanding of the devices and improve our ability to manufacture devices that meet all necessary performance goals.

### 2.2 SNSPD efficiency

As an ideal single photon detector will click once and only once when a single photon is incident on it, detection efficiency is one of the most discussed performance metrics of these devices. System detection efficiency, $\eta_{sde}$, is the overall probability that the detector will detect an incident photon, and is generally broken down as:

\[
\eta_{sde} = \eta_{coup} \times \eta_{abs} \times \eta_{click},
\]

while intrinsic device detection efficiency is defined as:

\[
\eta_{dde} = \eta_{abs} \times \eta_{click},
\]

where $\eta_{coup}$ is the fraction of light input to the system that is incident on the detector (the coupling efficiency), $\eta_{abs}$ is the probability that the detector will absorb a photon that is incident on it, and $\eta_{click}$ is the probability that the device will generate an output signal—that it will click—when it absorbs a photon. Clearly, $\eta_{dde}$ is simply $\eta_{sde}$ with the coupling efficiency divided out, so that $\eta_{dde} = \eta_{sde}$ only when $\eta_{coup} = 1$. It is worth discussing both $\eta_{sde}$ and $\eta_{dde}$ because each is useful in different contexts; $\eta_{dde}$ is used to compare device performance, while $\eta_{sde}$ is generally used in discussions of SNSPDs as part of an implementation of a photon-counting experiment. The literature is not consistent when it comes to naming what I have called system detection efficiency and intrinsic device detection efficiency, so it is generally advisable to be cautious when referring to device efficiencies and to specify what is being reported in all papers.
As this is a discussion of just the SNSPD itself, we will only concern ourselves with $\eta_{dde}$, in its two pieces $\eta_{abs}$ and $\eta_{click}$.

### 2.2.1 Improving device triggering efficiency

An SNSPD is triggered (to the best of our knowledge) through current crowding caused by absorption of a photon, which leads to regions with current exceeding $I_c$, Joule heating, and a fully resistive region [6]. Once a section of the device has gone entirely normal, the bias current flows through the bias resistor rather than the device, causing a voltage pulse across the resistor which is the measured click. Once there is no more current in the nanowire, the hot spot cools down and superconductivity can resume, resetting the device to click again. The precise mechanism for current crowding, and thus for what begins the click process, is poorly understood, though recent theoretical work has resulted in a model that can reliably predict device performance characteristics such as the $I_c$-dependent minimum photon energy and detection cutoff wavelengths [7]. Other than modifying the hot spot, the other way to improve $\eta_{click}$ is to ensure that by reducing the cross-sectional area available for supercurrent flow the current density in the current crowded regions will always exceed $I_c$.

It has been shown that detection efficiency improves when the bias current in the device is increased. However, that bias current is limited by the critical current of the device, which is determined by the spot in the device that has the lowest $I_c$. Thus, a single area in the detector that has $I_c = I_{c0}/2$, where $I_{c0}$ is the critical current for the rest of the device, would limit the entire device to running at $I_{c0}/2$. Furthermore, if the majority of the device will only trigger at $I_{c0}$ but it is limited to operating at 90% of $I_{c0}/2$, a hot spot must obstruct more than half the nanowire in order to cause the remaining superconducting region to contain current in excess of $I_{c0}$.

This single area with an anomalously suppressed $I_c$ is referred to as a ‘constriction.’ Constrictions can arise due to geometric features, such as corners or T-junctions, but they can also occur along straight sections of wire. Kerman et al. [22] made an experimental study of constrictions in patterned nanowires. They verified both optically and electrically that there can be large variation in performance between identically
fabricated detectors; the source of this performance variation is the aforementioned constrictions, which are point-like in nature (i.e. are very short in length). The most logical source of these variations would be errors in the lithographic patterning of the devices, in which any defects in the resist would result in a localized narrowing of the nanowire. However, extensive scanning electron microscopy inspection of the devices revealed no visible differences between devices, leading to the conclusion that the constrictions result either from material defects in the film or from thickness variations. As the quality of the resist and the uniformity of the films is only controllable to a limited extent—and is likely already very well controlled—these invisible constrictions are, for the moment, not a factor that can be controlled in device fabrication.

![Figure 2-2: Calculated supercurrent flows from Clem and Berggren [2]. The figure on the left is a simple 90° bend, and the figure on the right has an inner radius of curvature equal to half the nanowire width. It is clear from visual inspection that the current density is higher at the inner corner in both cases, but that the rounded corner results in a smaller increase in current density. Reprinted figures with permission from J. R. Clem and K. K. Berggren, Phys Rev B, 84, 174510 (2011). Copyright 2011 by the American Physical Society.](image)

A paper from Clem and Berggren [2] discusses a source of constrictions that is controllable: constrictions due to device geometry. Following work done 50 years ago by Hagedorn and Hall [13], Clem and Berggren calculated critical currents in thin superconducting strips with a variety of geometries, with the goal of investigating the possibility of current crowding due to sharp turns in the nanowires. Figure 2-
2 contains two figures from the Clem and Berggren paper, showing two possible geometries for a 90° bend. By going even farther and allowing the radius of curvature of the bend to go to infinity, it is possible to have no current crowding. They also made calculations of current flow in 180° bends, as this is highly relevant to SNSPD fabrication. They found that rounding the inner corner and extending the short section connecting the two wires in the direction of the wires resulted in reduced current crowding at the bends. Both of these design features can be seen in the device in figure 2-1.

2.2.2 Improving absorption efficiency

The other piece of \( \eta_{dde} \) is, of course, the probability that a photon incident on the device will be absorbed, \( \eta_{abs} \). The first devices fabricated were bare nanowires on a substrate, for which the absorption probability is simply the absorption probability of the material of the nanowires. This, among others, is the reason for the investigation into the optical properties of NbN in chapter 3. Newer devices include schemes to improve absorption of photons; here I will discuss one particular scheme that is used by our group, that of integrating a cavity on top of the nanowire [32]. This technique was also used by Marsili et al. [27] to achieve 93% system efficiency.

The nanowire itself covers perhaps half the area of the detector, and is only nanometers thick. Thus, even if NbN were a highly absorptive material, the odds of photon absorption are rather low. By integrating a cavity into the fabrication process, it is possible to maximize the intensity of light at the nanowire, thus maximizing the probability of photon absorption. It is reasonably simple to add a cavity to an already-fabricated SNSPD: the cavity material, often SiO\(_2\), must be deposited on top of the SNSPD at the appropriate thickness, after which a gold reflective layer is put on top. This gold layer is often sandwiched between very thin titanium layers, in order to improve adhesion. It is best to put the cavity on after the devices have been fabricated, as the best NbN films require a heated deposition and it is not certain that the gold layer would remain as deposited at these temperatures. Additionally, we usually illuminate our devices through the substrate, so the cavity must be on top.
of the nanowires.

Figures 2-3 and 2-4 show the results of modeling a single cell representing one nanowire, with appropriate boundary conditions to make it into a model of an infinite SNSPD. The optical stack modeled in these figures is, starting from the bottom, Si/2 nm Ti/120 nm Au/2 nm Ti/SiO_2 of varying thickness/4 nm 50% fill NbN nanowire/300 nm SiNx/2 nm fiber glue/optical fiber. This model was built to check the optimal cavity thickness for a device to be glued to a fiber through which incoming light is coupled. Modeling confirms that we do in fact want a cavity that is \((1/2+n)/2\) wavelengths long, and that an \(n/2\) wavelength cavity minimizes absorption; in both cases \(n\) is any positive integer.

Our lab does all modeling using room-temperature optical constants and assumes minimal thermal expansion of materials. Leviton and Frey [23] made measurements of the index of refraction, \(n\), of SiO_2 and observed that \(n\) changes by approximately 0.1% between 300 K and 30 K, while a paper from Frey et al. [8] shows that the refractive index of Si changes by approximately 0.8% over the same interval. Simulations done with the constants at 30 K and 300 K show a very small difference in the absorption peak location (varying cavity thickness for an SiO_2 cavity using 1550 nm photons): 805 nm at 30 K and 802 nm at 300 K. Thermal effects should also have minimal impact on cavity performance: the thermal expansion coefficient of SiO_2 is \(0.55 \times 10^{-6}/^{\circ}\text{C}\), indicating that a cavity built to be the correct length at room temperature will contract by less than 0.02% when brought down to cryogenic temperature. Thus, it seems that our assumption of room temperature constants will still result in effective cavities at cryogenic temperatures.
Figure 2-3: Electric fields inside an SNSPD with integrated cavity, as modeled with COMSOL. This cavity is 800 nm thick, at which there is an absorption maximum; this was expected, as this is one half of 3/2 wavelengths of 1550 nm light in SiO₂. The fact that the electric field is maximized right at the nanowire, as seen in the expanded inset, explains the absorption maximum.
Figure 2-4: Electric fields inside an SNSPD with integrated cavity, as modeled with COMSOL. This cavity is 500 nm thick, at which there is an absorption minimum; this was expected, as this is one half of a wavelength of 1550 nm light in SiO$_2$. The fact that the electric field is minimized right at the nanowire, as seen in the expanded inset, explains the absorption minimum.
Chapter 3

Optical characterization of ultra-thin niobium nitride films

Niobium nitride (NbN) is the material used by many groups, including our own, to manufacture the SNSPDs described in the previous chapter. Its high critical temperature allows devices made with NbN to be operated at liquid helium temperatures, and our lab is able to do all device-related processing in-house, making it an excellent choice for these detectors. The previous chapter also explored the ways in which efficiency can be improved through various device modifications. The absorption efficiency, discussed in section 2.2.2, is highly dependent on the optical properties of the device. That said, despite the fact that most of the materials used have been well-characterized optically, the NbN that actually does the absorbing has not yet been studied in any depth.

This chapter will cover all work relating to optically characterizing thin NbN films. I will describe the primary instrument used in characterization and explain why it is the optimal instrument for this study. I will explain the modeling process required to extract optical parameters from the measurements and the implications for non-optical film properties. I will present the results of this study, and then discuss how these results can be applied to our group’s fabrication processes.
3.1 Niobium nitride in general

NbN is a crystalline material that forms a cubic crystal, similar to that of NaCl. When grown using reactive sputtering, as is done in our group and in many others, the grain size and other properties of the material can be strongly influenced by the substrate on which the material is grown and by the deposition parameters. The parameters to deposit optimal NbN films have already been established for our sputtering system and are discussed in Andrew Dane's thesis [3]. For this particular exploration, the majority of films studied were deposited at room temperature on 1 cm square Si chips with 300 nm thermal oxide on top, diced from 6 inch wafers bought from MTI. Films were deposited in a variety of thicknesses and some identical films were deposited weeks apart, to study variation with film thickness and stability of our deposition process. Films were also deposited at 840°C on SiO₂ and AlN substrates to investigate variations in film properties with substrate material, but the results from measurements of these films are intriguing rather than definitive.

3.2 Variable angle spectral ellipsometry

Part of the reason that little work has been done on the optical properties of NbN is likely because it is difficult to measure optical properties of thin films, and even more difficult to measure optical properties of absorbing thin films. One must account for transmissions, reflections (multiple, internal, specular, diffuse), absorptions, and much more when measuring any material, and in thin films this is difficult due to the very short path length for interaction with the light. Additionally, given a very thick absorbing film it is possible to measure it as an infinite layer of just the top material, which dramatically simplifies the modeling to be done. In order to understand the results from a thin film the effects of the substrate material must be added to the model, thus increasing the number of variables and the complexity of the model.

The primary method used to measure optical properties of thin films is to use a Variable Angle Spectral Ellipsometer (VASE), or to perform Variable Angle Spectral
Ellipsometry, which has the same acronym. A VASE expands on the already large amount of information that can be measured by standard ellipsometry by also performing measurements at multiple incident angles (variable angle) and over a range of wavelengths (spectral).

Ellipsometry measures the change in polarization due to reflection or transmission off a material, specifically along the s- and p-directions. The p-direction is defined by the plane of incidence on the sample, and the s-direction is defined such that the p-direction, s-direction, and direction of propagation define a right-handed Cartesian coordinate system [19]. Once the s- and p-directions have been defined, we can easily express the polarization of any beam of light as a two-component Jones vector:

\[
\vec{E} = \begin{bmatrix} \vec{E}_p \\ \vec{E}_s \end{bmatrix}.
\] (3.1)

Having expressed the light as a Jones vector, we can now express all operations performed on the light with \(2 \times 2\) transfer matrices known as Jones matrices. This allows for easy evaluation of the effects of all the optical components in the instrument.

The VASE used in this study is a rotating analyzer ellipsometer. Light incident on the sample comes from a xenon lamp in a monochromator which is then sent through a polarizer, so that the polarization state of the light incident on the sample is known. After reflecting off the sample, the light goes through a continuously rotating analyzer before hitting the detector. The detector sees a sinusoidally varying intensity of light that depends on the polarization state of the light reflected off the sample.

We then need to evaluate the intensity of light incident on the detector. Knowing that the intensity of light is proportional to the electric field of that light, we will evaluate the electric field incident on the detector using the Jones formalism. In the Jones formalism, the expression for the beam of light incident on the detector can be expressed as

\[
E_D = [\text{Analyzer matrix}][\text{Sample matrix}][\text{Polarizer matrix}][\text{Input beam}],
\] (3.2)
after which we must simply find matrices for the analyzer, sample, and polarizer in order to evaluate the electric field at the detector.

Let us assume that the beam incident on the detector is p-polarized; we must then rotate this coordinate system back to the coordinate system of the ellipsometer, in which p-polarization is defined as the plane of incidence. If we call the angle between the polarizer axis and the plane of incidence $P$, then the polarizer matrix is simply a matrix describing rotation by $P$:

$$\text{Polarizer matrix} = \begin{bmatrix} \cos P & -\sin P \\ \sin P & \cos P \end{bmatrix}. \quad (3.3)$$

If the sample is isotropic and not too rough, its Jones matrix will be diagonal; the diagonal elements of the Jones matrix represent the change of amplitude and phase of the p- and s-polarized light, while the off-diagonal elements represent the transfer of energy from the p-component to the s-component, and vice versa [19]. For simplicity’s sake, let us assume that there is no transfer of energy. In this case, we can express the sample matrix as

$$\text{Sample matrix} = \begin{bmatrix} \tilde{R}_p & 0 \\ 0 & \tilde{R}_s \end{bmatrix}. \quad (3.4)$$

For the analyzer matrix, we need only be concerned with the rotation of the coordinate system to lie along the analyzer axis, since the rotation after the analyzer will drop out in the final evaluation of the square of the electrical field in order to get the intensity. We can express the analyzer matrix as:

$$\text{Analyzer matrix} = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} \cos A & \sin A \\ -\sin A & \cos A \end{bmatrix}, \quad (3.5)$$

where $A$ is the angle between the analyzer axis and the plane of incidence in the ellipsometer frame.
The final expression for the electric field at the detector is then easily assembled:

\[
E_D = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} \cos A & \sin A \\ -\sin A & \cos A \end{bmatrix} \begin{bmatrix} \tilde{R}_p & 0 \\ 0 & \tilde{R}_s \end{bmatrix} \begin{bmatrix} \cos P & -\sin P \\ \sin P & \cos P \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix}
\]  \hspace{1cm} (3.6)

and can be evaluated to find

\[
E_D = \begin{bmatrix} \tilde{R}_p \cos P \cos A + \tilde{R}_s \sin P \sin A \\ 0 \end{bmatrix}.
\]  \hspace{1cm} (3.7)

Once we have this expression for the electric field at the detector, the intensity at the detector is the square of \(E_D\). If we now define the complex ellipsometric parameter \(\tilde{\rho}\):

\[
\tilde{\rho} \equiv \frac{\tilde{R}_p}{\tilde{R}_s} = \tan \Psi e^{i\Delta},
\]  \hspace{1cm} (3.8)

we can show that

\[
I_D \propto |E_D|^2 = 1 + \alpha \cos 2A + \beta \sin 2A,
\]  \hspace{1cm} (3.9)

where \(\alpha\) and \(\beta\) are given by:

\[
\alpha = \frac{\tan^2 \Psi - \tan^2 P}{\tan^2 \Psi + \tan^2 P},
\]

\[
\beta = \frac{2 \tan \Psi \cos \Delta \tan P}{\tan^2 \Psi + \tan^2 P}.
\]  \hspace{1cm} (3.10)

Since we know that the analyzer angle \(A\) is actually a harmonic function of time, as it is rotating continuously, we can perform a Fourier transform on the experimentally determined detector signal to obtain the Fourier coefficients \(\alpha\) and \(\beta\), thus eliminating \(A\) as an experimental parameter. Having removed \(A\) from the picture, we can solve for \(\Psi\) and \(\Delta\) as functions of \(\alpha\), \(\beta\), and the polarizer angle \(P\), which gives us the equations used to extract \(\Psi\) and \(\Delta\) from the measured detector signal:

\[
\tan \Psi = \sqrt{\frac{1 + \alpha}{1 - \alpha}} |\tan P|
\]

\[
\cos \Delta = \frac{\beta}{\sqrt{1 - \alpha^2}} \tan P
\]  \hspace{1cm} (3.11)
The parameters $\Psi$ and $\Delta$ are what the VASE actually measures and reports to the user; these measurements are made at multiple incident angles and over a range of wavelengths. Taking measurements over a range of wavelengths allows for a particular dispersion relation to be enforced, if the material’s dispersion relation is known, and for Kramers-Kronig consistent parameters to be calculated. Acquiring these measurements at multiple incident angles provides more degrees of freedom and helps to generate a unique data set.

There are additional methods to further increase the measurement’s sensitivity to the sample, a major one of which is interference enhancement. From Hilfiker et al. [17], this method uses a thick dielectric film between the thin absorbing film and the thick substrate to increase the information contained in a series of multiple incident angle measurements. The additional information comes from variations in path length due to incident angle, and can reduce the correlation between optical constants and film thickness.

### 3.3 Modeling VASE data

In order to analyze ellipsometric data we require an accurate model of the measurement system, which encompasses both the instrument and the sample being measured; the analysis is highly sensitive to the optical constants used in the model. We can leverage this sensitivity in order to use a VASE to measure the optical constants of materials. A large base of optical constants has been accumulated in the history of ellipsometry, allowing for use of these accurate values in models to evaluate new materials. Most materials have a standard set of optical properties but others, such as TiN and TiO$_2$, have optical constants that depend on the deposition process.

An accurate model of the system allows for us to convert the measured $\Psi$ and $\Delta$ into optical constants. For the sake of discussion, let us examine the case of measurement of a bulk material in detail. We will assume the sample to be optically thick with no coatings or overlayers. Optical constants can be expressed as a complex dielectric function, $\tilde{\epsilon} = \epsilon_1 - i\epsilon_2$, or as a complex refractive index, $\tilde{n} = n - ik = \sqrt{\tilde{\epsilon}}$. 
Both descriptions contain the same information, and it is easy to convert between the two. We will look at both reflection and transmission since, even though reflection is the only measurement possible with the single-side polished substrates used for these measurements, transmission is relevant for the multi-layer samples in our study.

The Jones matrix representations of reflection and transmission are simply diagonal matrices:

\[
\begin{bmatrix}
\tilde{E}_p \\
\tilde{E}_s
\end{bmatrix}^{refl} = \begin{bmatrix}
\tilde{r}_p & 0 \\
0 & \tilde{r}_s
\end{bmatrix} \cdot \begin{bmatrix}
\tilde{E}_p \\
\tilde{E}_s
\end{bmatrix}^{inc},
\]

\[
\begin{bmatrix}
\tilde{E}_p \\
\tilde{E}_s
\end{bmatrix}^{trans} = \begin{bmatrix}
\tilde{i}_p & 0 \\
0 & \tilde{i}_s
\end{bmatrix} \cdot \begin{bmatrix}
\tilde{E}_p \\
\tilde{E}_s
\end{bmatrix}^{inc},
\]

so that the Fresnel reflection and transmission coefficients are:

\[
\tilde{r}_{p,s} \equiv \frac{\tilde{E}_{p,s}^{refl}}{\tilde{E}_{p,s}^{inc}}, \quad \tilde{i}_{p,s} \equiv \frac{\tilde{E}_{p,s}^{trans}}{\tilde{E}_{p,s}^{inc}}.
\]

We may now write the incident, reflected, and transmitted beams as follows:

\[
\tilde{E}_{p,s}^{inc}(\vec{r}, t) = \tilde{E}_{0p,s}^{inc} \exp\left(-i\frac{2\pi \tilde{n}_0 \cdot \vec{q}_{inc} \cdot \vec{r}}{\lambda}\right) \exp i\omega t,
\]

\[
\tilde{E}_{p,s}^{refl}(\vec{r}, t) = \tilde{E}_{0p,s}^{refl} \exp\left(-i\frac{2\pi \tilde{n}_0 \cdot \vec{q}_{refl} \cdot \vec{r}}{\lambda}\right) \exp i\omega t,
\]

\[
\tilde{E}_{p,s}^{trans}(\vec{r}, t) = \tilde{E}_{0p,s}^{trans} \exp\left(-i\frac{2\pi \tilde{n}_0 \cdot \vec{q}_{trans} \cdot \vec{r}}{\lambda}\right) \exp i\omega t,
\]

in which the direction of propagation is contained in the unit vector $\tilde{\hat{q}}$. We can then plug these expressions for the incident, transmitted, and reflected fields into equation 3.14, during which we require the tangential components of $\tilde{\vec{E}}$ and $\tilde{\vec{H}}$ and the normal components of $\tilde{\vec{D}}$ and $\tilde{\vec{B}}$ to be continuous across the interface due to boundary conditions [12].

The first interesting result from this is, of course, that the angle of reflection is equal to the angle of incidence. The second result is Snell’s law:

\[
\tilde{n}_0 \sin \phi_0 = \tilde{n}_1 \sin \phi_1,
\]
which states that the relationship between the angle of incidence, $\phi_0$, and the angle of propagation of the transmitted beam, $\phi_1$, depends on the indices of refraction of the incident material, $n_0$, and the sample, $n_1$. In the case that $n_1$ is complex $\phi_1$ will also be complex, leading to some absorption of the transmitted beam.

Finally, we can extract expressions for the Fresnel reflection and transmission coefficients for the interface at the surface of the bulk sample:

\begin{align*}
\tilde{r}_p &= \frac{\tilde{n}_1 \cos \phi_0 - \tilde{n}_0 \cos \phi_1}{\tilde{n}_1 \cos \phi_0 + \tilde{n}_0 \cos \phi_1}, \\
\tilde{r}_s &= \frac{\tilde{n}_0 \cos \phi_0 - \tilde{n}_1 \cos \phi_1}{\tilde{n}_0 \cos \phi_0 + \tilde{n}_1 \cos \phi_1}, \\
\tilde{t}_p &= \frac{2\tilde{n}_0 \cos \phi_0}{\tilde{n}_1 \cos \phi_0 + \tilde{n}_0 \cos \phi_1}, \\
\tilde{t}_s &= \frac{2\tilde{n}_0 \cos \phi_0}{\tilde{n}_0 \cos \phi_0 + \tilde{n}_1 \cos \phi_1}.
\end{align*}

In order to evaluate $\Psi$ and $\Delta$ in the bulk sample case, we insert equations 3.19 and 3.20 into the ellipsometric equation 3.8.

Of course, evaluating multi-layer films is not quite this simple, but it follows from the same principles. The main difficulty in evaluating multi-layer films comes from the presence of multiple internal reflected and transmitted beams, as seen in figure 3-1. The previous derivation is locally valid at all interfaces, so evaluating multi-layer films simply requires applying the previous results to every interface. This ends up not being particularly simple, however, so it is at this point that we allow the computer to take over. The VASE measurement software is equipped to perform the calculations described above; it is also able to model the material itself to generate optical parameters that are used to calculate $\Psi$ and $\Delta$ and to iteratively optimize these optical constants to fit the measured data.

It is this modeling of optical parameters that is the particularly complicated component of evaluating VASE data, and for which the VASE software is very well suited. The program contains the optical properties of many common materials and also has the ability to model unknown materials. In our case we used the General Oscillator
Figure 3-1: Multiple reflected and transmitted beams for the case of a single film on an optically thick substrate. The presence of two layers, as is the case with our samples, results in a doubling of the number of outgoing reflected beams at each of the single beams in the one-layer case.

(Chemical engineer) Layer available in the WVASE software to model NbN, which is not commonly available in the material libraries for this instrument. Of primary importance when discussing the results from the GenOsc layer is that a VASE is capable of making measurements that no other instrument can make, and thus in many cases there is no way to truly confirm that the model generated is the correct one, only that it fits the measured data. As there is no way to verify a model, it is generally assumed that if a model fits, it is the correct one. In all cases where other measurement methods can be used, they have supported the results of the VASE analysis.

The GenOsc layer models the dielectric function of a material using a linear summation of real and complex terms, or ‘oscillators,’ all of which are a function of wavelength, inverse wavelength, or photon energy. The forms of these functions depend on the type of oscillator chosen as components for the GenOsc layer. In our case we had a purely real offset added to $\epsilon_1$, a Lorentz oscillator, a rho-tau Drude oscillator, and a Gaussian oscillator. A Lorentz oscillator consists of a Lorentz model of a single bound electron, modeled as a mass on a spring; this oscillator is used as the basis for the other oscillators used in our GenOsc layer. The rho-tau Drude oscilla-
tor describes free carrier effects and consists of a Lorentz oscillator with no restoring force. The Gaussian oscillator is a collection of Lorentz oscillators that produce a Gaussian line shape in $\varepsilon_2$ with a Kramers-Kronig consistent line shape in $\varepsilon_1$. The model was initially generated from a sample with $\sim$10 nm of NbN on $\sim$300 nm of SiO$_2$ on silicon.

The creation of a model for a particular material is very important, but it is not the final step in the process. The initial model then needs to be decorrelated, meaning that variables must be fixed so that the fitting process will always generate the same final result. The variables set to fixed values during decorrelation are those that are statistically the most correlated to the others, meaning that large changes in their values will not lead to large changes in the model. A model that has not been decorrelated will either not converge in a reasonable number of iterations, or will converge to different but very similar values depending on the initial conditions. A decorrelated model will converge to the same result independent (within reason) of the initial parameters of the model and will converge in a sensible number of iterations. In some cases using a decorrelated model from another sample with nearly the same properties (usually everything is the same except the thickness of the NbN film) is the only way to get the model to converge in a reasonable number of iterations. It was generally possible to use a single decorrelated model for all film thicknesses; this decorrelated model produced nearly identical results to models decorrelated individually for all samples.

The model that was used for all the data reported here was developed for NbN deposited at room temperature on SiO$_2$ and works quite well for that particular optical stack [35]. It was also used to model NbN deposited on AlN, with less success. This lack of success is likely a combination of the NbN structure being changed by the different substrate and the thinness of the few films available for measurement. A better model for NbN on AlN could be developed using a sample with a thicker NbN layer.
3.4 Reporting NbN optical constants

Figure 3-2 shows the calculated optical properties of three films deposited for 100 s and three deposited for 250 s; one of each was deposited 2 weeks apart, to investigate the stability of the deposition process over time. From the figure we can see that the optical properties are really quite stable over time, though there is less variation in the thicker film. Table 3.1 reports how various film properties vary for each set of three. It is interesting to note that while the thicker films vary less in their optical properties and thickness, both sets of films vary by the same amount in their superconducting properties.

Figure 3-2: Optical properties of 6 films; for this data set a pair of 100 s and 250 s films was deposited three times, each 2 weeks apart. We see that though both sets of data are reasonably similar, the 250 s films are more consistent than the 100 s films. See table 3.1 for the variation in parameters between films.

Figure 3-3 shows the optical properties of a set of films deposited for times ranging between 75 and 480 s. All films other than the 480 s film were deposited over the course of 2 days, and the 480 s film was deposited a month later to provide an
additional data point. Also shown in the figure is the data our group has been using for the last few years in device simulations, which come from a film sent to J.A. Wollam for measurement; the precise parameters of that film are unknown, though it is likely a thick, heated deposition on SiN_x. From the figure we can see that there are three data sets—the old data, SPE924, and SPE925—that do not match up with the rest of the data. That the old data does not match is not surprising, since it was deposited with different parameters and on a different substrate. That the two thinnest films (1.8 nm and 3 nm) do not line up with all the other films is surprising and an interesting result. The 150 s – 480 s depositions vary by 10% at 1550 nm, and if we exclude the 480 s film, which was deposited a month later than the rest, they vary by only 6%.

The sudden change in optical properties of films thinner than 6 nm (the 150 s film is approximately 6 nm thick) would seem to indicate some sort of phase change at that thickness. In chapter 4 we discuss a scaling law for thin film superconductors and find that these thinner films do not follow that scaling law, as seen in figure 4-2. However, other than their not fitting the scaling law, we can see that there are no dramatic changes in superconducting properties with thickness (see figure 4-1), so the nature of this phase change is not clear. It is possible that it is related to the percolation threshold of NbN, but we were not able to perform any measurements to confirm or contradict that hypothesis.

Figure 3-4 shows the calculated optical properties of NbN films deposited on both SiO_2 and AlN, both heated and not heated. It is interesting to note that the shape of the \( \epsilon_1 \) and \( \epsilon_2 \) curves are very different for the two thicknesses of NbN on AlN,
Figure 3-3: Optical properties of films over a range of thicknesses, nearly all deposited within days of each other, and the optical properties the group has been using for the last few years.
Figure 3-4: Optical properties of heated depositions on SiO$_2$ and AlN compared to room temperature depositions on SiO$_2$ of similar thicknesses.
possibly indicating that the model developed for use with NbN on SiO₂ is not ideal for NbN on AlN; no such shape change was seen with changing thickness in the films considered in figure 3-3. Other than that it is difficult to make conclusions about these results due to how thin the heated NbN on SiO₂ film is; this film was intended to bridge between the room temperature NbN on SiO₂ measurements and the heated NbN on AlN measurements. It does seem clear that there is a significant difference in optical properties for the two different substrates, but it is not possible to make any quantitative conclusions from this data.

Figure 3-5: Plot of optical properties of thin NbN films from Semenov et al [33]. Reprinted figure with permission from A. Semenov et al., Phys. Rev. B 80, 054510 (2009). Copyright 2009 by the American Physical Society.

Semenov et al. [33] published one of the few papers available on the optical properties of thin NbN films. They tested films grown in heated depositions on sapphire substrates; doing a heated deposition on a crystalline substrate like sapphire should result in a film with fewer grain boundaries and generally a more uniform crystal structure than the majority of the films we measured, which were deposited at room temperature on an amorphous substrate. Semenov et al. optimized the NbN composition for maximum $T_c$ at each thickness, so that unlike our films the recipe for each thickness is different. Their results for optical properties are shown in figure 3-5. The most notable differences between our results and theirs is that their $\epsilon_1$ decreases
monotonically for all thicknesses, while in our films deposited on SiO$_2$ the $\epsilon_1$ decreases until around 800 nm at which point it begins to increase, as seen in figure 3-3. Our films deposited on AlN—which is a crystalline substrate like sapphire—do have $\epsilon_1$ values that generally decrease monotonically, as seen in figure 3-4. In particular, this monotonic decrease holds for the thicker film deposited on AlN, for which we have more confidence in the reported optical constants. There seems to be no significant differences in the reported values of $\epsilon_2$.

Though I was unable to create my own model for NbN optical properties, I was able to acquire and modify a model for gold originally created by Joel Yang, a former member of this group; we can use this model to make qualitative conclusions about the difference between our data and that from Semenov et al. Using a Drude model with Lorentz corrections, Yang was able to reproduce experimentally measured optical properties of gold reasonably accurately. The Drude model, which models free electron oscillations in metals, generally shows a monotonically decreasing trend in $\epsilon_1$ and a monotonically increasing trend in $\epsilon_2$. By adding in Lorentz terms we can add interband transitions to the model. The Lorentz correction terms are introduced at frequencies corresponding to the frequencies at which the atom will start to absorb light.

To use the gold model to compare the two data sets, we will modify it to reflect the differences between our data and that from Semenov et al. The results of these modifications are seen in figure 3-6. It was not possible to generate a positive slope in $\epsilon_1$, but it was possible to cause it to decrease much more slowly, while making minimal changes to $\epsilon_2$, as is seen in our data sets. To achieve this shift in the constants we lowered the plasma frequency, which is analogous to lowering the concentration of free carriers, and increased the damping frequency, which in practice represents an increase in scattering centers. Both of these modifications are reasonable when we consider the differences between the two sets of films. The films measured by Semenov et al. were deposited heated and on crystalline substrates, so they should have larger grain sizes and thus fewer scattering centers, and should also have a more regular crystalline structure, which would increase the concentration of free carriers. Thus
Figure 3-6: These plots are the results of Drude and Drude-Lorentz modeling of the optical properties of gold overlaid on experimental data from Palik [25]. The dashed red curve is a pure Drude model, the solid red curve is a Drude-Lorentz model optimized to fit the experimental data, and the black dotted curve is a version of the Drude-Lorentz model modified to reflect the changes between our data and that from Semenov et al.
by investigating a model of the optical properties of gold we are able to assert that some of the difference between our measurements and those from Semenov et al. are reasonable when we consider the deposition processes used.

![Figure 3-7: This plot contains the measured thickness vs deposition time for all films deposited, with the films that were deposited within a two-day window, SPE924–929, indicated. There are also three fits to different subsets of the data points, as well as the estimated deposition time for a 5 nm thick film using our standard assumption of linear growth starting from time t = 0.](image)

Having a set of films with closely varying thicknesses also allowed us to investigate the assumption that film growth is linear starting at time $t = 0$, which is used in our group and others to extrapolate between thicker films that are measurable and the thinner films that are needed for device fabrication but are difficult to measure. Figure 3-7 contains the measured thicknesses of all films deposited on SiO$_2$ plotted against their deposition time, along with fits to certain subsets of the data and a point found with our usual method of determining thin film deposition. We see that though the measured thickness of the films follows a linear trend, this line does not pass through the origin. In the case of the fit through all data points, the fit intercepts the y-axis at $-0.95$ nm, and when we exclude the 480 s film the y-intercept is at approximately $-1.5$ nm. In all fits, growth does not appear to start until approximately 50 s after...
the deposition has started. This is a significant difference from the usual assumption that growth starts at time $t = 0$. Using the 480 s film and the origin as our only data point, the calculated time for a 5 nm thick film is 125 s; from the fits, a 5 nm thick film should take approximately 140 s—a difference of 10%—and a 125 s film should be about 4.3 nm thick, 15% thinner than the goal of 5 nm.

### 3.5 Applications of these results

As the group is mostly interested in fabricating devices, we must also discuss applications of the results discussed above. This study was initially driven by a desire to confirm the optical constants used in modeling our devices, but other interesting results have come from the data acquired.

While fabricating devices it is very important to have consistent properties between fabrication runs. This means that we must be able to produce identical films weeks or even months apart. As seen in figure 3-3, the optical properties of films are quite consistent for all films thicker than 6 nm; figure 4-1 shows that there is also little variation in superconducting properties above 6 nm. So it would seem that in order to ensure that films have the same properties when they are deposited at different times, the films used should be 6 nm or thicker. Our group currently makes devices on 5 nm thick films; it is possible that 5 nm films would fall in with the 6 nm and thicker films, as we have no data point for 5 nm, but it could also be that our group could improve device consistency by moving to slightly thicker films.

We can see in figure 3-4, as well as in comparing figures 3-3 and 3-5, that films deposited with different parameters and on different substrates have different optical properties. It might be possible to optimize the film properties to a particular wavelength, or even improve the absorption by better index-matching to the optical cavity.

Our study of the optical properties of ultra-thin NbN films has led to the conclusion that there is some significant shift in film properties at a critical thickness, and that substrate and deposition parameters such as heat have noticeable effects on the
optical properties of the films. In line with the existence of a critical thickness, the properties of thicker films are more consistent when deposited at different times than those of thinner films.
Chapter 4

Investigating a scaling law for superconductors

A paper by Ivry et al. from within the Berggren lab collected data from the nearly 50 years of published measurements of thin film superconductors in the hope of establishing a universal relationship between $d$, the film thickness, $T_c$, the critical temperature, and $R_s$, the sheet resistance, for thin superconducting films [20]. Without any understanding of how these properties interact, our understanding of the onset of superconductivity and the development of miniaturized superconducting devices is hindered. Hotspot formation relies on the superconducting-normal transition, as does the rest of how an SNSPD is triggered; $T_c$, $R_s$, and $d$ are all implicated in the performance metrics discussed in chapter 2, and improving them (raising $T_c$ and stabilizing $R_s$ and $d$) would result in better control of fabrication and of device properties. Ivry et al. reported that the mentioned quantities scale according to

$$dT_c = AR_s^{-B},$$

where $d$, $T_c$, and $R_s$ are as indicated above and $A$ and $B$ are fitting parameters with appropriate units.

The set of NbN films discussed in chapter 3 in terms of optical properties also represents the first time that our lab has deposited a set of films of varying thicknesses.
with the same recipe over only a few days, and so is an excellent data set to test the scaling law against. The short time scale over which these films was deposited means that there should be minimal variation other than thickness (and any related shifts) between the films. In addition, all the NbN films evaluated by Ivry et al. were grown on crystalline substrates and thus should be epitaxial, meaning that their crystal structure is guided by the crystal structure of the substrate they are grown on; our films are grown on amorphous SiO₂ and thus have no particular expected crystal structure or orientation.

![Graphs showing metallic and superconducting behavior of thin NbN films on SiO₂.](image)

Figure 4-1: Metallic and superconducting behavior of thin NbN films on SiO₂. Top left is $T_c$, critical temperature, vs $d$, film thickness; top right is $T_c$ vs $R_s$, the sheet resistance; bottom is resistivity, $R_s \cdot d$, vs $d$. Though it does appear that it would be possible to fit these plots with various functions, Ivry et al. showed that these fits do not apply to other materials and thus are not universal.

As in the paper from Ivry et al., figure 4-1 includes plots of various combinations of superconducting and electrical properties of the films. It is not possible to find a universal fit to these parameters for all the data sets used, despite the fact that it
Figure 4-2: Using the scaling law from Ivry et al [20]: $d \cdot T_c = A \cdot R_s^{-B}$. In this case, $A = 36160$ and $B = 1.092$. Note that it fits quite well other than the four rightmost points, which means that it fits well for films thicker than 5 nm.

looks as if, for a single material, they can all be fit to something. Figure 4-2 shows the fit of our data to the scaling law. It looks to be a good fit to all points other than the rightmost four, which represent the 100 and 75 second films; the attentive reader will recall that, in chapter 3, we saw that these are the films whose optical properties do not line up with all the other films. It is therefore not entirely surprising that the superconducting properties of these films do not fit the others.

Figure 4-3 is a figure from the supplemental material for Ivry et al. It contains all the data gathered for use in the paper on a log-log scale. A certain amount of this data was not used in the paper for various reasons, but let us specifically consider the datasets that deviate from the power law fit at high $R_s$, those that decrease faster than that fit. In the supplemental material, it is suggested that this may be due to suppression of $T_c$ by the proximity effect, as all the films in which this occurs were deposited on conducting substrates. However, this behavior is also demonstrated
Figure 4-3: A plot of all data used by Ivry et al, taken from the supplementary information to that paper. We are particularly interested in the datasets that clearly deviate from being a straight line; these datasets include ▲ Al from Liu et al. [24], + Pb from Haviland et al. [14], ▼, and Bi from Haviland et al. [14]. See Ivry et al. [20] for references for all other data points.

by our NbN films deposited on SiO2, which is not conducting and thus cannot be proximitizing the superconductor.

Reading the supplemental material, it is clear that all data points that did not follow the power law scaling were excluded from the data set used in the main body of the paper. Looking specifically at the three data sets indicated in figure 4-3, a different rationale was used to exclude data points from each data set. The Al films from Liu et al. generally show $d \cdot T_c(R_s)$ decreasing monotonically, but more slowly than the power law in equation 4.1; it is indicated that this might be due to the large uncertainties on $d$, $T_c$, and $R_s$, though no clear discussion of error on the published values is evident in the paper from Liu et al. The extracted $T_c$ values match up well between extracted values for $d$ and $R_s$. The other available data for Al thin films
does seem to cover the same thickness of films, but the $R_0$ for the films from Liu et al. is three times larger for the thinnest films, and the $T_c$ of these films is much lower. As other data sets for Al were available and do follow the scaling law, it seems that some unaccounted for effect has dramatically altered the properties of the films from Liu et al., and thus this data set was excluded by virtue of its not fitting equation 4.1.

In the case of Pb and Bi films from Haviland et al., it is only some of the points that do not follow the power law. For the Pb films, the films whose values deviate from equation 4.1 are all thinner than the nominal lattice constant of Pb. Excluding these films seems logical given that this scaling law assumes 2D superconductivity of a continuous film; if the films are thinner than the lattice constant, it is reasonable to assume that they are not homogeneous, not continuous, or both. The Bi films show a (moderate) increase of error in data extraction for $d < 0.85$ nm, leading to the eight thinnest films being excluded from the data analyzed in the paper. In fact, six of these eight films are within extraction error of the power law fit, so that by including extraction error nearly all of this data set fits equation 4.1. In the case of these two sets of films, there is a clear reason to exclude the data from consideration in the paper, one which is unrelated to their fit to equation 4.1.

The deviation from the power law for these films could also, as suggested, be due to some systematic measurement error, since the three data sets that are specified in the caption for figure 4-3 come from the same lab and a similar time period. However, if this is the case, it is strange that the Bi and Pb films fit the scaling law well up to a certain point, after which they deviate. The film thicknesses were determined by monitoring the changes in resonant frequency of a quartz crystal as a function of the thickness of the deposited films. The thickness calculation was done assuming standard bulk crystal densities, so it is possible that some deviation from these values occurs at very small thicknesses. This is particularly likely in the case of the Pb films, as films thinner than the nominal lattice constant are likely to have crystal properties that are not those of the bulk crystal.

We then come to my NbN films. Film thickness in this case was measured as part
of the optical parameter calculations, but the thickness measurements will generally be accurate for thinner films than it is possible to get accurate optical constants for; this is because for very thin films, interference due to internal reflections is visible even if the path length is so short as to provide minimal opportunity for the optical parameters to effect the probe light. That said, a significant assumption of the VASE modeling is that the film is uniform; the beam spot size is on the order of millimeters, so any variations in film thickness will be averaged out. Thus, if a substrate is 50% covered with a 4 nm thick film, and the other 50% is bare substrate, this calculation would indicate that the entire film is 2 nm thick. This returns us to the debate from chapter 3 regarding percolation threshold; if it is the case that these films are not uniform but are rather semi-isolated islets, this could explain the thinner films not matching the thicker ones. However, looking at figure 4-1 it is clear that the resistivity does not change dramatically for thinner films, which would seem to indicate that they are structurally similar to the thicker films.

If we consider the reasons given for excluding the films discussed above from the scaling law paper, none of them seem to fit my films. It is not possible that my insulating substrate is proximitizing the films. The nominal lattice parameter for NbN is approximately 0.44 nm, an order of magnitude thinner than my films [39]. As this is my own data there are no errors due to data extraction, and the measurement errors in $T_c$ and $d$ do not reach the power law fit line.

While it seems clear that there is some mechanism affecting the properties of these superconducting films at high $R_s$, it is also apparent that this mechanism cannot be solely attributed to the proximity effect, nor to any identifiable measurement error. It must be emphasized that the scaling law from Ivry et al. does fit the majority of data sets considered by the authors, as well as the data set from this work for lower values of $R_s$, and thus would seem to be a useful metric in those cases. It is only for higher $R_s$ values that the data deviate from the power law, and in most cases this correlates to the thinnest films. As with many other aspects of superconducting thin films, the mechanism for this deviation requires further study.
Chapter 5

Niobium titanium nitride thin films

Though niobium nitride (NbN) has been very successfully used by many groups, including our own, to manufacture superconducting nanodevices, other materials have recently come into use. One of these is tungsten silicide (WSi), which has been found to be more flexible and forgiving than NbN due to its amorphous, homogeneously disordered structure; a major disadvantage of WSi, however, is its low critical temperature, which means that WSi devices require operating temperatures below 2 K [27]. Another material that has been infrequently used but could be interesting is niobium titanium nitride, NbTiN, which is of course NbN with Ti added. NbTiN, like NbN, has a cubic lattice structure and grows well as an epitaxial film from a lattice-matched substrate, though overall NbTiN films are less affected by the substrate than NbN films are [40]. NbTiN exhibits higher critical temperatures than NbN and generally has lower kinetic inductance and smaller sheet resistance [1, 30].

As our lab has very successfully used NbN for devices and we have a Ti target in our sputtering system, it was decided that determining an optimal recipe for NbTiN with our system would be of interest for future device development. NbTiN can be operated at liquid helium temperatures and can be managed entirely in-house, as NbN can, and it is possible that shifting to NbTiN would result in improved device performance with minimal trouble.
5.1 NbTiN properties

Though NbN and NbTiN were first investigated in thin film form at around the same time, NbTiN was left to languish mostly uninvestigated until relatively recently and was not used to make SNSPDs until 2008 by Dorenbos et al [5], eight years after SNSPDs were first demonstrated by Gol'tsman et al. Despite assertions from Dorenbos et al. that they were able to decrease dark counts by an order of magnitude simply by switching to NbTiN from NbN, as well as the fact that NbTiN has a higher critical temperature and lower resistivity than NbN, NbTiN did not come into general use and remains less frequently used as a material for SNSPD fabrication.

The properties of reactively sputtered thin NbTiN films were first investigated in the 1960's by Bell et al. [1] and Gavaler et al. [9], among others. Both groups demonstrated higher critical temperature for bulk and thin film NbTiN than they had achieved in NbN, though their definition of 'thin film' means on the order of hundreds of nm. They also demonstrated the possibility of adjusting the superconducting properties by changing the Nb:Ti ratio in the film.

More recent work has explored the parameters that are of interest when making superconducting detectors. These parameters include the material's lattice-matching to substrates useful for detector fabrication and implementation, high critical temperature, low sheet resistance, low kinetic inductance, and the ability to repeatably deposit high-quality thin films. As already mentioned, NbN fulfills many of these key metrics, but it seems that NbTiN can improve on most if not all of them.

Both NbN and NbTiN have a cubic lattice structure, and produce devices with the best performance using films with large grain sizes. One way to achieve large grain size is to deposit epitaxial films on a substrate whose lattice constant matches that of the material to be deposited. NbN is generally deposited on sapphire or MgO for epitaxial growth, though neither are a perfect lattice match. NbTiN has a slightly smaller lattice constant than NbN and as such is very well matched to MgO [40]. A better lattice match results in fewer grain boundaries and thus a more uniform film.

Higher critical temperature and lower resistivity were visible in bulk NbTiN when
compared to NbN and have carried over to the ultra-thin films required for SNSPD fabrication. A paper by Miki et al. in 2009 [30] explicitly compares detectors made with NbN and NbTiN. They found that for thin films (<10 nm) they saw higher critical temperature and lower resistivity at 20 K in NbTiN films than in NbN films. They also saw a smaller sheet inductance in SNSPDs made from NbTiN than those made from NbN; the NbTiN sheet inductance was about 25% lower. Lower inductance would allow for the manufacture of larger devices with similar reset times to current devices, as the reset time is controlled by the inductance of the device, and there is a minimum inductance necessary to avoid latching.

Adding Ti to the system has other benefits for film properties. The critical temperature of NbN films is highly dependent on the nitrogen stoichiometry and is generally lowered in the presence of vacancies in the crystal lattice. Ti is a good nitrogen getter and, in addition to increasing the conductivity of the film, reduces vacancies in the crystal lattice. Reduced vacancies mean a more uniform film, which improves the repeatability of film properties [40]. The properties of NbTiN films are also, despite their crystallinity, relatively less sensitive to the substrate they are deposited on than those of NbN films. Finally, it is possible to adjust the conductivity of the film by changing the Ti content. While this also changes the superconducting properties, it is an adjustment that is not possible with NbN [21].

5.2 NbTiN recipe optimization

The majority of groups using NbTiN deposit their films by reactive sputtering from an NbTi alloy target; this target is often either 80:20 or 70:30 Nb:Ti. Our sputtering system already had Nb and Ti targets installed, so rather than buy a new NbTi target—and need to install it and bake out the chamber—it was decided to perform this optimization with the system as it was, so with separate Nb and Ti targets. This allowed for variation in the ratio of Nb to Ti as well as variation in the nitrogen content, rather than restricting us to only varying the nitrogen ratio with a fixed Nb:Ti stoichiometry; ultimately the Nb to Ti ratio is what was explored in this study.
Development of the NbTiN recipe began with our optimized recipe for NbN on SiO$_2$, as it contains parameters that are known to be able to maintain the plasma for sputtering and allowed the deposited films to be compared to older films from this system. All films studied were long depositions—480 s—so that their thickness could be measured by x-ray reflectivity (XRR) and in the hopes of seeing the maximum possible $T_c$. The standard NbN recipe requires 400 mA on the Nb target, 26.5 sccm Ar and 6 sccm N$_2$ at various pressures—just Ar at 30 mTorr to spark the plasma, Ar at 2.5 mTorr to clean the target surface, and Ar + N$_2$ at 2.5 mTorr for the actual sputtering—and optionally involves a bias on the substrate. The substrate onto which we are sputtering is mounted in a rotating chuck set at 40 mm on its micrometer. Films were deposited by reactive magnetron sputtering inside of an AJA Inc ATC Orion sputtering system; this system is described in Andrew Dane’s masters thesis [3]. To deposit NbTiN the Nb target is still DC biased, but the Ti target is RF biased. It is unknown if this configuration introduces any particularities to the deposited films, though none were evident.

The first set of films was deposited with varying Ti content, along with a 'zero' Ti film to be used as a reference. The power on the Ti target was varied in 50 W steps from zero up to 300 W, the maximum possible in the system. The reference film was deposited with 100 W on the Ti target but with the shutters on the Ti target kept closed; this is because the peak power seen on the Nb target during the depositions was unusually low compared to that seen when depositing NbN films, and we thought that it might be due to the use of the Ti target. By having power across the Ti target while keeping the shutters closed we saw a similar peak power on the Nb target as in the NbTiN films for our reference film, but were still able to deposit an NbN film. Despite the lower peak power on the Nb target, the film properties were similar to those of an NbN film deposited with the Ti target off.

We measured the superconducting properties of the deposited films with a properly equipped cryostat (explained in detail in Andrew Dane’s thesis [3]), and the film thicknesses were measured by XRR using the Rigaku SmartLab, a tool available for use in the CMSE at MIT. The cryostat measures the resistance of each film as a
Figure 5-1: Output from the control software of the cryostat used to measure $T_c$. Once given the voltage and temperature as a function of time, it determines the resistance as a function of temperature and evaluates the superconducting transition’s position and width. The resistance at 20 K is also displayed for use in calculating RRR.

function of temperature, from which it is possible to extract the critical temperature of the films. Figure 5-1 shows the data recorded with this device, from which $T_c$, $\delta T_c$ (the width of the superconducting transition), and RRR are extracted. Figures 5-2 and 5-3 show the recorded XRR data and the fit performed to determine fit thickness. All films were modeled starting from an initial model of $\sim 30$ nm of Nb, NbN, or TiN on $\sim 300$ nm of SiO$_2$ on thick Si; the optical and physical parameters of the top layer and the thickness of the middle layer were allowed to vary. As there were no parameters available for NbTiN in the XRR fit library, some films were fit with multiple starting materials, to ensure that the results were not strongly affected by the initial conditions. Note that while the fit in figure 5-3 is not as good as that in figure 5-2, the period of the fringes—the primary indicator of film thickness—is accurately reproduced.

The first set of films demonstrated that films with higher Ti content had higher $T_c$ and RRR (residual resistance ratio) while maintaining a similar resistivity, all of
Figure 5-2: SPE860 fit to XRR data, starting from niobium constants; the initial model was \( \sim 30 \text{ nm} \) of Nb on \( \sim 300 \text{ nm} \) of SiO\(_2\) on thick Si. The modeled thickness when starting from NbN constants was 0.06\% smaller than the thickness found with Nb constants.

Figure 5-3: SPE889 fit to XRR data, starting from NbN constants; the initial model was \( \sim 30 \text{ nm} \) of NbN on \( \sim 300 \text{ nm} \) of SiO\(_2\) on thick Si. The modeled thickness when starting with TiN constants was 0.2\% thinner than the NbN value.
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<th>bias (W)</th>
<th>film thickness (nm)</th>
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<th>$R_s$ (Ω)</th>
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$^o$ This film was deposited with 100 W on the Ti target but with the shutters closed, to check for effects related to using both the Ti and Nb targets at the same time.

$^*$ Thickness was not measured for these films, as their superconducting properties were less desirable than other films.

$^t$ These films were deposited with 8 sccm N$_2$; all other films were deposited with 6 sccm N$_2$.

$^\square$ Noisy $T_c$ data for this film meant it was not possible to measure a resistance at 20 K.

$^\dagger$ These films were deposited with pressure in the chamber at 3 mTorr; all other films used 2.5 mTorr.

Table 5.1: Deposition parameters and measured thickness and superconducting properties of all thick NbTiN films deposited for this study. For the purpose of making the table fit, the columns for N$_2$ content and chamber pressure were omitted, with the four films that used unusual values in one of these fields as indicated. All depositions were 480 seconds long.
which indicate higher quality films, or at least films that are more desirable for use in our devices. However, all these films had a high sheet resistance, which is not something we look for in films. Previous work had taught us that depositing with a bias on the substrate leads to lower resistance films, so another partial set of films was deposited with a substrate bias; this set of biased films only covered the higher Ti powers, as the unbiased films indicated that the lower Ti content films have less desirable properties. Films were also deposited with more N\textsubscript{2} in the system (N\textsubscript{2} at 8 sccm rather than 6) in an attempt to balance out the additional metal in the system; the Ti replaces Nb in the crystal lattice, so adding Ti to the deposition may require additional N\textsubscript{2} to maintain the original nitrogen content in the film. Finally, two films were deposited with the maximum Ti power but with lower Nb content, in case our maximum Ti power was not high enough to hit the optimum Ti content. Table 5.1 contains all the deposition parameters of the films deposited for testing and their measured properties.

5.3 NbTiN film properties

To facilitate understanding, I present the data in table 5.1 in graphical form.

Figure 5-4 contains $T\text{c}$ vs Ti content for films deposited with the standard NbN recipe with Ti added, both biased and not biased, overlaid on data from Bell et al. [1]. The Ti content was not directly measured for this plot. Rather, the Ti content was calculated by assuming that any thickness difference from SPE864, which had zero Ti content, was made up of pure TiN; essentially the NbTiN was modeled as a set amount of NbN with a variable amount of TiN on top. This calculation was only possible for the non-biased set of films, as there was no zero Ti content film for the biased films; with the biased films it was assumed that film stoichiometry depends only on target current and N\textsubscript{2} availability and thus the same Ti content values as the unbiased films were used to plot the biased films. This estimation of Ti content makes many questionable assumptions but seems to have been adequate for our purposes. We ultimately do not need to know precisely how much Ti is in a given film, only
Figure 5-4: This plot is the measured $T_c$ of the more complete sets of films vs an estimate of their Ti content based on film thickness, overlaid on a plot taken from Bell et al. [1] that shows variation of the $T_c$ of NbTiN with Ti content of the films. Even without optimized parameters, my films do a reasonable job of following the trend seen by Bell et al.
that it has optimal properties. This plot is the reason that films SPE935 and SPE936 were deposited, as it was not clear if we had achieved the Ti content for maximum $T_c$, which looks to be around 36%. This plot clearly shows that we were not able to achieve the maximum possible $T_c$ for NbTiN films (which we are aware of as we were not able to exceed the $T_c$ achieved with NbN in this same system, which should be possible), though our films follow the same trend as those from Bell et al. It is also possible that achieving their values will not be possible, since their definition of ‘thin film’ is on the order of hundreds of nm, while our ‘thin films’ are tens of nm thick. That said, hundreds of nm thick NbTiN films were still thin enough to show a dramatic shift from the $T_c$ curve of bulk NbTiN.

![Graph showing measured thickness vs power on the Ti target for all films for which I have those measurements, with a linear fit for the series that have multiple entries.](image)

Figure 5-5: Measured thickness vs power on the Ti target for all films for which I have those measurements, with a linear fit for the series that have multiple entries.

Figure 5-5 shows the measured thickness of all films for which thickness was measured vs power on the Ti target. As expected, adding a bias to the substrate results in thinner films, as we are then sputtering off the substrate surface even as we are depositing material on it. That the films with lower Nb content are even thinner
than the first two sets of films is also expected, as sputtering yield generally decreases for higher sputtering pressure, and it was necessary to sputter the lower Nb-content films at 3.0 mTorr rather than the standard 2.5 mTorr used for all other films, as the plasma would not stay ignited at the lower pressure. The fact that the lower Nb content films are significantly thinner than the other Ti-at-300-W films is worth keeping in mind for the next plot, as even at these thicknesses $T_c$ can vary as a function of film thickness [40].

![Figure 5-6: Critical temperature vs power on the Ti target for all thick NbTiN films.](image)

The biased films are clearly superior to the non-biased films, in particular since they are thinner than their non-biased counterparts. The comparison to the $N_2$-rich films and the Nb-poor films is less clear, because the Nb-poor films are thinner and thus will have a lower $T_c$ regardless of its possible maximum value.

Figure 5-6 is the critical temperature, $T_c$, of all films plotted against the power on the Ti target. It is clear that the biased films are superior in this metric, and that 6 sccm $N_2$ is better than 8 sccm $N_2$, despite the fact that there should overall be more metal in the system with the addition of the Ti target. It is worth looking back at figure 5-5 and remembering that the two films with lower Nb content ( and
are significantly thinner than the films with full Nb content (\(\circ\) and \(\triangledown\)). Though there should be less variation in \(T_c\) with thickness at the values of these films, we still expect some variation in \(T_c\). It is likely that the lower Nb content films would have higher \(T_c\) than the biased, full Nb content films were they the same thickness.

![Graph](image.png)

Figure 5-7: Resistivity \((R_s \cdot d)\) vs power on the Ti target. \(\times\) and \(\triangle\) are older films deposited with the same parameters but with the Ti target completely off; these are different from the power = 0 points, because those actually had 100 W on the Ti target but had the shutters closed.

Figure 5-7 contains the film resistivity, \(R_s \cdot d\), vs power on the Ti target. Two additional points are added from films not in table 5.1, \(\times\) and \(\triangle\), which are NbN films deposited with the same parameters as the N\(_2\) at 6 sccm films but with no Ti in the system. This is distinct from the ‘zero’ Ti film listed in the above table, as this film was deposited with power on the Ti target but with the shutters closed so that there was no Ti in the deposited film but the Ti target was still active. As expected, the biased films have a much lower resistivity; this is because depositing with a bias generally results in more uniform films, and it is nonuniformities that
increase resistivity. It is interesting that the resistivity is approximately the same for all Ti contents within a particular set of films, as other works have indicated that resistivity can be controlled by Ti content. It is possible that this effect requires higher Ti content than we have been able to achieve. It is also very interesting that all three films deposited with the Ti at 300 W and with a bias have very similar resistivities, despite their differing Nb content.

![Graph](image)

**Figure 5-8:** RRR vs power on the Ti target for all films deposited.

In figure 5-8 we see the residual resistance ratio, $\text{RRR} = \frac{R_{300K}}{R_{20K}}$, vs Ti target power. High RRR is generally an indicator of film quality and metallic behavior [16]. Both these assessments seem to agree with the data, as the biased films have higher RRR than the non-biased films, and the films with greater Ti content have greater RRR than those with a lower Ti content. Other NbN films produced by our lab indicate that the RRR tends to peak at about 0.85 for a heated deposition on SiO$_2$. This is approximately what was achieved at room temperature for a non-biased NbTiN film with the Ti at 300 W, and less than all NbTiN films deposited with a
bias.

After analyzing all the films deposited with the standard NbN content (SPE860–SPE890), thin films were deposited to test parameters on films that would actually be useful for device fabrication. The parameters used to deposit the thin films were those used for SPE878 and SPE881, the two best thick films produced. The deposition time was selected to generate a 5 nm thick film, assuming linear growth starting at $t = 0$. The resulting films were generally unremarkable in their properties and were similar to NbN films deposited under similar conditions, other than having a higher RRR; the higher RRR is to be expected, as by adding Ti to the film we render it more metallic. Without making devices with these films we cannot evaluate their performance in the areas of reset time, dark counts, or presence or lack of constrictions. As no thin films were made with lower Nb content, it is possible (very possible, even) that these recipes would result in better properties, and that a further optimized recipe would ultimately surpass the NbN recipe currently in use.
Chapter 6

Conclusions and questions

As this thesis has touched on many different topics, this final chapter will collect the important results as well as the questions that have arisen during this research.

6.1 NbN optical parameters

The most surprising result from the NbN optical study was the existence of a critical thickness, above which the optical properties of our films stabilized. There is no evidence for this critical thickness when we look at plots of the sheet resistance or critical temperature, nor has this been reported in the few papers available on NbN optical properties. This critical thickness is likely the reason why 250 s films show much less variation between deposition runs than 100 s films do, as small changes in thickness for the thinner films can lead to significant changes in the optical properties. Though at this time we do not require films as thin as those that fall far below the critical thickness, understanding the origins of the critical thickness could lead to a better understanding of how the NbN films grow and their superconducting properties. Studying these films using electron microscopy or some other method that would allow observation of their structure and layout could help give insights into the origins of the critical thickness and their growth patterns. As this critical thickness also seems to affect the scaling law discussed below, it may be that the critical thickness is evidence of a phase shift that has so far gone unnoticed in this material.
Less surprising is the evidence of strong effects of the substrate on the optical properties of the deposited NbN. In this study we were only able to make qualitative comparisons, but the shape of the $\epsilon_1$ and $\epsilon_2$ curves are quite different between our films on SiO$_2$ and those on AlN, and our $\epsilon_1$ curves on SiO$_2$ are also significantly different from those reported by Semenov et al. on sapphire substrates. Work on this particular question was limited by our modeling ability with the VASE, but could prove to be of interest for optimizing optical properties of NbN films for particular devices and wavelengths.

Of great interest for further investigation is, of course, quantifying the effect of the substrate on the NbN thin film and determining if the observed changes are only evident when comparing amorphous substrates to crystalline substrates or if there are also observable differences between different crystalline substrates. This investigation would also touch on how the crystal structure of the films changes their optical properties, as films grown on amorphous vs crystalline substrates and films grown on crystalline substrates with different degrees of lattice mismatch to NbN will show different crystal structures.

The successful use of the VASE also opens the door to doing similar studies of other materials at both room temperature and at cryogenic temperature, which is where these materials are actually used. It is generally assumed that the superconducting transition does not cause any shift in optical properties, since this transition happens at a much smaller energy scale than those of the photons the film is interacting with, but no published data for these measurements is available. Regarding which other materials might be studied, WSi and NbTiN are both used to make superconducting detectors and thus their optical properties are of interest for the same reasons that those of NbN are of interest. In particular, it is possible that different materials that show similar cryogenic properties, as is the case with NbN and NbTiN, could have different optical properties that make them more or less suited for use in devices at particular wavelengths.
6.2 Universal scaling law

We were able to show that our set of films fit the scaling law published by Ivry et al. quite well, but only above the critical thickness observed in optical testing. Below this critical thickness, \( d \cdot T_e(R_s) \) decreases more quickly than the power law fit, similarly to some other films processed for the paper published by Ivry et al. but ultimately excluded from the data set used in the main body of the paper. Ivry et al. proposed that the excluded data sets deviated from the fit due to their being proximitized by a conducting substrate, but it seems that this cannot be the only explanation. Some of the data sets were excluded for reasons other than their not fitting the power law fit, and our own films were deposited on an insulating substrate and thus cannot be subject to the proximity effect. While it does seem clear that there is some effect causing these films to deviate from the published scaling law, there must be reasons other than solely the proximity effect for this deviation.

As mentioned above, it is of interest to gain a better understanding of the origins of the critical thickness, which was only visible in optical measurements and in the context of this scaling law. Better understanding the origins of the critical thickness may allow for a deeper understanding of why the thinnest films do not follow the scaling law, which could further our understanding of how the scaling law breaks down.

It would also be interesting to further test the scaling law, both in the materials that for some reason did not fit the law and in any materials that were not available for testing when the paper was published. More absolute methods of measuring thickness than those used in the available data, which consisted of observing the resonant frequency of a quartz crystal or of assuming linear growth, could allow for more confidence in the fit, or lack thereof, of any new data to the scaling law. If possible, deposition of more films on conducting substrates could probe the effect, or lack thereof, of any changes in the scaling law fit due to the proximity effect.
6.3 NbTiN thin films

Starting from our lab's established room-temperature NbN recipe, it was reasonably simple to deposit NbTiN films that matched the superconducting properties of the best NbN we are able to fabricate. The ease with which we equalled the properties of NbN indicates that it should be possible to deposit NbTiN films that have superior properties to those we are currently seeing in NbN.

The study reported in chapter 5 fully investigated the properties of NbTiN films with the amount of Nb used in our normal room-temperature NbN recipe, but did not explore the possibilities of lower Nb content with maximum Ti content, nor did it attempt to compare films of similar thickness between different levels of Nb content. The lower Nb content films are significantly thinner than those with the standard Nb content, and as such are likely to have lower $T_c$ simply because they are thinner. In order to make a good comparison between different Nb:Ti stoichiometries, the films tested should all be of similar thicknesses. The lower Nb content films seem to have the best properties of all films studied, and should be investigated further.

Another extension to the NbTiN study is measurement of the optical properties of the films. Though the VASE study performed on NbN was very informative, it was a non-trivial task to perform the same study on NbTiN given time limitations. The lack of a general model for NbN means that there is no simple starting point for NbTiN analysis, and the model created for chapter 3 was not easily modified to work with NbTiN. TiN is also not a simple starting point, as it is a material that exhibits a range of optical constants depending on how it is deposited; this variable starting point means that any modeling of NbTiN based on TiN is also a non-trivial task. That said, performing a study of the optical properties of NbTiN would be of great interest for modeling their potential use in SNSPDs and to observe any similarities between NbTiN and NbN in how they vary with all the parameters of interest in the NbN study.
Bibliography


