Materials for epitaxial superconducting heterostructures:  

Nb, NbN and NbO/Nb

Hugh Conlon  
15318341

Supervisor: Prof. Igor Shvets

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School of Physics
Trinity College Dublin
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Abstract

Josephson Junctions are junctions that operate under the Josephson effect, the tunnelling of electrons through a non-superconducting layer between two superconducting layers. They are popular candidates for the realisation of quantum bits due to the low dissipation inherent to superconductors making long coherence times possible. In practice, two level system defects present in the barrier layer at the nano and atomic-scale can interact with qubits leading to decoherence. The ultimate goal of this project is to successfully implement new Josephson Junction architectures and designs. In service of this goal, the aims of this report are twofold. The first is to investigate the formation of a crystalline NbO barrier layer on an epitaxial Nb film that could replace the traditional AlO_x barrier that currently limits junction performance. The second is to investigate the fabrication of a superconducting δ-NbN film for use in a spin-triplet superconductor.

In the first half of the first section of this study, Nb films were grown on c-plane Al_2O_3 and the relationship between the film’s thickness and its superconducting properties was investigated. It was found that as thickness decreased, transition temperatures decreased as well as was expected. The formation of an oxide layer on the surface of the films that were exposed to atmosphere was noted through XRR measurements. This oxide layer was utilized in the second half of this section where the formation of a NbO(111)-terminated Nb(110) thin film was attempted. The thin film was subjected to anneals of ~700°C. X-ray photoelectron spectroscopy measurements confirmed the reduction of surface oxides such as Nb_2O_3 and NbO_2 to NbO but also the formation of NbC. Removal of NbC via Ar sputtering was unsuccessful. A higher temperature anneal (~2000°C) may remove the carbide and lead to the formation of a NbO-terminated Nb thin film.

In the second half of this study, the growth of superconducting δ-NbN thin films on c-plane Al_2O_3 via DC magnetron sputtering and their potential application in a spin triplet superconducting heterostructure were investigated. X-ray diffraction patterns revealed that under nitrogenation during growth led to the formation of γ-Nb_4N_3 and β-Nb_2N mixed phase films which were not superconducting. An increase in N_2 during growth saw a shift in phase from γ-Nb_4N_3 to δ-NbN, however β-Nb_2N was still present and the films were still not superconducting. The mixture of phases present in the films may be affecting their superconducting properties. A subsequent post anneal of the first film did not return a superconducting film. The phase of this film post anneal could not be successfully determined due to issues with the XRD apparatus. Revisions of the growth process such as the modulation of Ar gas flow or growth on a different substrate may lead to the realisation of superconducting δ-NbN.

Keywords: Superconductivity, Transition Temperature, Niobium, Josephson Junction, Al_2O_3, Niobium Oxide, Niobium Nitride
Abbreviations

- *JJ* - Josephson Junction
- *TLS* - Two Level System
- *ATLAS* - Atomic Terrace Low Angle Shadowing
- *MBE* - Molecular Beam Epitaxy
- *XRD* - X-ray Diffraction
- *XRR* - X-ray Reflectivity
- *XPS* - X-ray Photoelectron Spectroscopy
- *AFM* - Atomic Force Microscopy
- *LEED* - Low Energy Electron Diffraction
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Introduction

When two superconductors are in proximity to each other with a barrier between them, a current is produced that flows continuously between them without the need to apply a voltage. This phenomenon, named the "Josephson effect", was first discovered by Brian David Josephson in 1962 and devices that utilise this effect, "Josephson Junctions", were developed in the following year. Since then, there has been a growing interest in the fundamental physics and applications of this effect.

Josephson junctions are good candidates for the construction of quantum bits (qubits) for a quantum computer. The state of a standard binary digit, or bit, is always 0 or 1. However, the general state of a qubit can be a coherent superposition of both. Qubits can be coherently controlled and the time over which a qubit behaves in this fashion and is useful for quantum information applications, is known as the "coherence time". In principle, superconductors have inherently low dissipation that should lead to high coherence times. In reality, defects in the crystal structure of the barrier layer will lead to decoherence and a reduced coherence time. The reliance on an oxide barrier layer will limit the progress that can be made in this emerging field. It is the aim of this project to reimagine the barrier layer entirely and revise the standard Josephson Junction architecture.

Chapter 1 is divided into two sections; the first half reviews the history of superconductivity starting with its discovery in 1911 and then details the subsequent developments that laid the groundwork for the Josephson effect. The second half describes the Josephson effect, Josephson junctions and the defects in the crystal structure of the barrier layer that lead to decoherence. There is also discussion about potential new Josephson Junction architectures.

Chapter 2 deals with the variety of experimental apparatus that were utilised throughout this project. The operation of the equipment used for fabrication of superconducting thin films is discussed as well as a plethora of characterisation devices including the atomic force microscope, the x-ray diffractometer and the x-ray photoelectron spectrometer.

Chapter 3 is split into two halves; the first discussing the fabrication of superconducting niobium thin films on sapphire substrates and the effect the thickness of the film has on its superconducting properties; the second reviews the production of a niobium oxide layer on single crystal niobium and details attempts to replicate that on thin film niobium for use as a barrier layer.

Chapter 4 reviews the developments of the emerging technologies of spin-triplet superconductors and discusses attempts to fabricate a niobium nitride film for use in such a device.

Chapter 5 concludes this report by presenting further discussion and future work based on the results of this project.
1 Background and Theory

And all this science, I don’t understand,
It’s just my job five days a week.

Elton John
Rocket Man

1.1 Superconductivity

1.1.1 Zero Resistivity

The phenomenon of superconductivity was first discovered in 1911 by H. Kamerlingh Onnes. Kamerlingh Onnes observed that mercury would transition from a finite resistance in the normal state to \( R = 0 \Omega \) as the temperature of the metal was reduced towards 0K \([1]\). Notably, the resistance does not fall smoothly as anticipated as the temperature tends towards 0K, but instead drops sharply at 4K and below this temperature mercury exhibits zero resistance (and hence, zero resistivity). Kamerlingh Onnes recognized that below 4K, mercury passed into a new state which we know as the "superconducting state". This transition to the superconducting state occurs at a critical temperature \( T_c \) which is material specific. Kamerlingh Onnes also demonstrated this effect in other metals such as tin \([2]\) and lead \([3]\).

Figure 1: Superconductivity in a mercury sample. Adapted from Kamerlingh Onnes (1911) \([1]\)

Although it is not possible to directly measure zero resistance or resistivity, measurement of an upper bound to resistance was possible. As early as 1914, Kamerlingh Onnes was inves-
tigating the decay of a current in a closed superconducting circuit. The reasoning behind such measurements was that if there was a resistance present in the circuit, the current would give rise to Joule heat. If no decay is detected, the observation time of the experiment and the geometry of the circuit would allow for a calculation of the upper limit.

If a resistance, $R$, exists within a superconducting loop with inductance $L$, in the presence of a current $I = I(t)$, conservation of energy requires

$$\frac{d}{dt} \left( \frac{1}{2} LI^2 \right) + RI^2 = 0$$

(1)

with the solution being

$$I(t) = I_0 e^{-\frac{R}{L} t}$$

(2)

where $I_0$ is the initial current at $t = 0$ and $I(t)$ is the current at time $t$. The decay time of the current and corresponding magnetic induction, $B$, is $\tau = L/R$. The instruments used to measure the decay of current and magnetic field can only determine the maximum amounts by which these have decayed. In reality, the decay may be a lot lower, hence we estimate the decay of the current and magnetic field at a timestep of $t_1$ as such

$$\delta I > I_0 - I(t_1) = I_0 \left(1 - e^{-\frac{R}{L} t_1}\right)$$

(3)

$$\delta B > B_0 - B(t_1) = B_0 \left(1 - e^{-\frac{R}{L} t_1}\right)$$

(4)

Therefore,

$$\frac{\delta I}{I_0} = \frac{\delta B}{B_0} > \left(1 - e^{-\frac{R}{L} t_1}\right)$$

(5)

Solving for $R$, we find the upper bound to be

$$R < \frac{L}{t_1} \ln \left(1 - \frac{\delta B}{B_0}\right) = \frac{L}{t_1} \ln \left(1 - \frac{\delta I}{I_0}\right)$$

(6)

where all quantities on the right can be determined from experiment.

Assuming we are using a single loop with radius $r$ made from a wire of diameter $a$ such that $r \gg a$, the inductance parameter $L$ can be given as

$$L \approx \mu_0 r \ln(r/a)$$

(7)

This derivation closely follows Chapter 1.2 of *Superconductivity: Physics and Applications* by K. Fosheim and A. Sudbø.
where \( \mu_0 \) is the permeability of free space \((4\pi \times 10^{-7} \text{Vs/Am})\). Our expression for the upper bound becomes

\[
R < -\frac{\mu_0 r \ln(r/a)}{t_1} \ln \left(1 - \frac{\delta B}{B_0}\right)
\]  

Assuming we have a single loop of Al wire with \( a = 0.5\text{mm}, r = 5\text{mm}, \) an instrumental resolution that gives us \( \frac{\delta B}{B_0} = 10^{-5} \) and an observation time of a year, \( t_1 \approx 3 \times 10^7 \text{s}, \) we get a resolution upper bound of \( R < 10^{-19}\Omega. \)

The upper limit of resistivity can then be found from

\[
\rho < 10^{-19} \frac{A}{l} \approx 2.5 \times 10^{-25}\Omega\text{m}
\]  

where \( A \) is the area and \( l \) the length and cross section of wire in the loop. In this specific case, the resistivity at \( T_c \) has dropped by a factor of \( 10^{13} \) compared to the normal resistivity, \( \rho_n, \) of Al at helium temperatures \((2.5 \times 10^{-12}\Omega\text{m})\).^3

It would seem justified that the resistivity of a metal disappears in the superconducting state and hence we have perfect DC conductivity (i.e. infinite electrical conductivity) below \( T_c. \) However, it alone is not sufficient to explain the electromagnetic behaviour of a superconductor.

1.1.2 The Meissner Effect

Prior to 1933, the electromagnetic properties of the superconducting state were considered with perfect conductivity as the only basic characteristic. Meissner and Ochsenfeld discovered that a magnetic field applied to a superconducting body above \( T_c \) would be expelled from the body after cooling below \( T_c. \)^6

Consider the constitutive equation for a magnetic body in the superconducting state

\[
B = \mu_0 (H + M) = 0
\]

Where \( H \) is the applied field and \( M \) is the magnetization of the material, i.e. the density of magnetic dipole moments in a material. From this we can see that \( M = -H \) and therefore, the susceptibility takes on the value of a perfect diamagnet

\[
\chi = \frac{dM}{dH} = -1
\]

Naturally this implies that the relative permeability of the material \( \kappa = 0 \) as \( \kappa = 1 + \chi. \)
When the material cools below $T_c$, shielding currents arise on the surface. The field generated due to these currents will exactly cancel with the induced field and the field on the outside will add with the induced field. Hence we observe an expulsion of the B-field within the superconductor and an increased field on the outside as seen in Fig. 2.

![Diagram](image.png)

Figure 2: An illustration of the Meissner effect in a superconductor. On the left, the magnetic field lines penetrate the superconductor while it is above $T_c$. On the right, the magnetic flux is expelled from the interior of the superconductor. The highest density of flux lines is found around the equator. At the poles there is a lower density than before the field expulsion.

This discovery was a major step forward in understanding the electromagnetic behaviour of a superconductor. The state is uniquely defined by the values of the thermodynamic variables $T$ and applied field $H$, independent of how the state was reached. This would not be possible if the only characteristic of superconductivity was perfect conductivity below $T_c$.

Consider a sample cooled to below $T_c$ in a zero-applied field that exhibits zero resistivity. If a field is then applied to this sample, Lenz’ law requires that currents are to be generated in the sample to screen the field out. As $\rho = 0$, this situation will persist and there will be no field inside the superconductor. If we then remove the field, Lenz’ law demands that the flux remain constant in the sample and so the currents will diminish to zero. There will be no magnetic flux within the sample.

Next, consider a second identical sample that has a field applied to it at room temperature, allowing the flux to penetrate it. As it is cooled down to $T_c$, Lenz’ law will require the flux inside to remain constant. If the external field is removed, spontaneous current will arise on the surface to satisfy Lenz’ law. As $\rho = 0$, this situation will persist and flux will remain inside the superconductor.

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This is dependent on the type of superconductor. This is discussed in more detail in 1.1.8.
Despite both of these scenarios having the same $T$ and $H$, the final states are quite different. This abnormality arises because of the assumption that the only property the superconductor gained on cooling to below $T_c$ was perfect conductivity. In a real superconductor, both scenarios would end in the same final state owing to the Meissner Effect. We can conclude from this fact, that superconductivity is a thermodynamic state and not just a state characterized by zero resistivity.

1.1.3 The London Equations

In 1935, the London brothers proposed a phenomenological theory to describe some of the properties of superconductors. Although these equations cannot be derived rigorously, they have a strong motivation underpinning them both in classical and quantum mechanics.

To derive the first London Equation, the Londons considered the Drude-Lorentz equation of motion for electrons in a normal metal

$$m \frac{\partial v}{\partial t} = -eE - \frac{mv}{\tau} \tag{12}$$

Here $v$ is the drift velocity of the charge carrier of charge $e$, $m$ is its mass, $E$ is the local electric field, and $\tau$ is a phenomenological relaxation time which describes how long it takes the scattering to bring the velocity of the carrier to zero. In a superconductor with a density of superconducting carriers, $n_s$, we consider the scenario, $\tau \to \infty$. In other words, the electrons freely accelerate without dissipation such that $\tau \to \infty$. In other words, the electrons freely accelerate without dissipation such that (12) now becomes

$$m \frac{\partial v}{\partial t} = -eE \tag{13}$$

The current density carried by these electrons is given by

$$j_s = -en_s v_s \tag{14}$$

Thus (13) can be written as

$$\frac{\partial j_s}{\partial t} = \frac{n_e e^2}{m} E \tag{15}$$

This is the first London Equation and it describes perfect conductivity.

Derivation of the second London Equation involves taking the curl of both sides of the first.

$$\frac{\partial}{\partial t} \nabla \times j_s = \frac{n_e e^2}{m} \nabla \times E \tag{16}$$

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See Chapter 1.2 *Introduction to Superconductivity* by M. Tinkham

The following derivations closely follows Chapter 34 of *Solid State Physics* by N.W. Ashcroft and N.D. Mermin and Chapters 1.2 and 2.1 of Tinkham’s *Introduction to Superconductivity*. 
From Faraday’s Law, we get

$$\frac{\partial}{\partial t} \nabla \times \mathbf{j}_s = -\frac{n_se^2}{m} \frac{\partial \mathbf{B}}{\partial t}$$

(17)

Rearranging this gives us the London’s second law

$$\frac{\partial}{\partial t} \left( \nabla \times \mathbf{j}_s + \frac{n_se^2}{m} \mathbf{B} \right) = 0$$

(18)

This does not predict the Meissner Effect but instead the diamagnetic response to time-varying fields. The Londons hypothesized that the behaviour of superconductors could be explained by making the bracketed term equal to zero.

As previously stated, it is also possible to justify the London equations by considering quantum mechanics. F. London first emphasized this in 1951.\(^\text{10}\) Utilizing a specific vector potential, \(\mathbf{A}\), which is fixed to the London gauge, the canonical momentum operator can be defined as

$$\mathbf{p} = m\mathbf{v} + e\mathbf{A}$$

(19)

London argued that in the absence of an applied field (i.e. like in a superconductor), one would expect the canonical momentum to be zero (as shown in a theory of Bloch’s\(^\text{8}\)). With this in mind, rearranging (19) gives us

$$\langle \mathbf{v}_s \rangle = -\frac{e\mathbf{A}}{m}$$

(20)

This will hold if we assume that the wavefunction of the superconducting electrons remains "rigid" and retains its ground state form. We can now rewrite (14) replacing \(\mathbf{v}_s\) with its expectation value

$$\mathbf{j}_s = -en_s\langle \mathbf{v}_s \rangle = -\frac{n_seA}{m}$$

(21)

Taking the time derivative of this will return (15) and taking the curl of it will give (18). As stated, \(\mathbf{A}\) is not gauge invariant and will only be treated as a current density if fixed to the London gauge. The London gauge specifies that \(\nabla \cdot \mathbf{A} = 0\), \(\mathbf{A} = 0\) in the superconducting bulk, and \(\mathbf{A} \cdot \hat{n} = 0\), where \(\hat{n}\) is the normal vector at the superconductor’s surface. The London theory gives a sound explanation of zero resistivity and the Meissner effect but it cannot explain all physical phenomena of a superconductor. The need for a microscopic mechanism that gives rise to this wave-function rigidity and, ultimately, to the superconducting state was apparent.
### 1.1.4 London Penetration Depth

An important superconducting property arises when we manipulate by applying Ampère’s Law

\[ \nabla \times \mathbf{B} = \mu_0 \mathbf{j}, \tag{22} \]

where \( \mu_0 \) is the magnetic permeability of free space. Taking the curl of that yields

\[ \nabla \times (\nabla \times \mathbf{B}) = \mu_0 (\nabla \times \mathbf{j}). \tag{23} \]

Applying that to (18) gives us

\[ \nabla \times (\nabla \times \mathbf{B}) = -\frac{\mu_0 n_s e^2}{m} \mathbf{B} \tag{24} \]

However \( \nabla \times (\nabla \times \mathbf{B}) = \nabla (\nabla \cdot \mathbf{B}) - \nabla^2 \mathbf{B} \). Applying that relation give us

\[ \nabla (\nabla \cdot \mathbf{B}) - \nabla^2 \mathbf{B} = -\frac{\mu_0 n_s e^2}{m} \mathbf{B} \tag{25} \]

But Gauss’ Law for Magnetism states \( \nabla \cdot \mathbf{B} = 0 \), therefore

\[ \nabla^2 \mathbf{B} = \frac{\mu_0 n_s e^2}{m} \mathbf{B} \tag{26} \]

Applying the Helmholtz equation for a magnetic field, \( \nabla^2 \mathbf{B} = \mathbf{B}/\lambda^2 \), we get

\[ \nabla^2 \mathbf{B} - \frac{\mathbf{B}}{\lambda^2} = 0 \tag{27} \]

where \( \lambda \) is the London Penetration Depth

\[ \lambda_L \equiv \sqrt{\frac{m}{\mu_0 n_s e^2}} \tag{28} \]

It characterizes the distance to which a magnetic field penetrates into a superconductor and becomes equal to \( e^{-1} \) times that of the magnetic field at the surface of the superconductor.

### 1.1.5 BCS Theory and Cooper Pairs

Prior to the development of a microscopic theory, there were several key experimental discoveries that verified the existence of a previously postulated band gap between the ground state and the quasi-particle excitations of the system. A quasi-particle excitation is not an actual particle but rather a concept used to describe a collective behaviour of a group of particles that can be treated as if they were a single particle.
The concept of this energy gap was suggested by several theoreticians but the first quantitative experimental evidence was discovered by Corak et al.\textsuperscript{11} Precise measurements of the electronic specific heat of the superconducting state, $C_{es}$, showed that below $T_c$ the heat was dominated by an exponential dependence

$$C_{es} = \gamma T_c ae^{-bT_c/T} \quad (29)$$

where the electronic specific heat of the normal state, $C_{en}$, is given by $C_{en} = \gamma T$ and $a$ and $b$ are numerical constants, approximately equal to 10 and 1.5 respectively. The implication of this exponential dependence is that the minimum excitation energy per particle is about $1.5kT_c$.

Almost simultaneously in 1950, Maxwell\textsuperscript{12} and Reynolds\textsuperscript{13} discovered the effect of nuclear mass on $T_c$. By studying $T_c$ of materials containing a different element isotope, it was shown that $T_c$ changes as $M^{-1/2}$, where $M$ is the mass of the isotope. As $M$ is only related to the ions forming the lattice, this experiment indicated that the lattice itself (and by extension the phonons) play a key role in the formation of the superconducting state. Additionally, measurements of electromagnetic absorption in the region of $\hbar \nu \sim kT_c$ indicated a gap width of about three to four times $kT_c$\textsuperscript{14}

A microscopic theory that underpinned the superconducting state was first proposed by Bardeen, Cooper and Schrieffer (BCS) in 1951\textsuperscript{15} The idea behind BCS theory is that at sufficiently low temperatures, electrons near the Fermi surface become unstable against the formation of Cooper pairs. Cooper pairs are electrons (or other fermions) bound together at low temperatures which will occur in the presence of an attractive potential no matter how weak.\textsuperscript{16} These can be visualized easily (if simplistically) with an electron moving through a conductor which then attracts positive charges in the lattice. The deformation of the lattice will attract an electron to the area of higher positive charge density. The two electrons correlate and create a Cooper pair. In a superconductor, there is a condensation (i.e. all Cooper pairs have the same energy) because the Cooper pair quasi particle is a boson (spin zero) and hence the Pauli exclusion principle does not apply.
One of the key predictions of BCS theory is that a minimum energy, $E_g = 2\Delta(T)$, is required to break a Cooper pair into two quasi-particle excitations. The superconducting energy gap, $\Delta(T)$, is expected to increase from 0 to $T_c$ to a limiting value such that for $T \ll T_c$

$$E_g(0) = 2\Delta(0) = 3.528k_B T_c$$

where $\Delta(0)$ is the superconducting energy gap at zero temperature and $k_B$ is the Boltzmann constant. This result is as expected from the experimental results previously mentioned.

### 1.1.6 Ginzburg-Landau Theory and Coherence Length

The other major development in superconducting theory at this time was the Ginzburg-Landau (GL) theory which focused on superconducting electrons. Ginzburg and Landau asserted that the superconducting state could be characterized by a complex order parameter $\psi(r)$, which would vanish above $T_c$. The magnitude of $\psi$ would measure the degree of superconducting order at a position $r$ below $T_c$. In terms of BCS theory, the order parameter can be viewed as a one-particle wavefunction describing the position of the center of mass of a Cooper pair. Unlike electrons which have spin-$\frac{1}{2}$ and must obey the Pauli Exclusion principle, Cooper pairs have a total spin of an integer (either 0 or 1) and so act as a composite boson. Since all Cooper pairs are in the same two electron state, it is only necessary to use a single function.

The basic postulate of GL theory is that if $\psi$ is small enough and varies slowly in space, the

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Footnote:

$^*$The derivation of this value is largely outside the scope of this thesis but is covered in excellent detail in Chapter 4 of *Superconductivity: Physics and Applications* by K. Fossheim and A. Sudbø.
free energy density $F$ can be expanded in a series of the form

$$F = F_n + \alpha |\psi|^2 + \frac{\beta}{2} |\psi|^4 + \frac{1}{2m^*}|(-i\hbar\nabla - 2eA)|\psi|^2 + \frac{|B|^2}{2\mu_0}$$  \hspace{1cm} (31)$$

where $F_n$ is the free energy of the normal phase, $\alpha$ and $\beta$ are phenomenological parameters, $m^*$ is the effective mass, $e$ is the charge of an electron, $\hbar$ represents the reduced Planck’s constant, and $A$ is the magnetic vector potential, such that $B = \nabla \times A$. By minimizing the free energy with respect to variations in the order parameter and vector potential, we get the Ginzburg-Landau equations

$$\alpha \psi + \beta |\psi|^2 \psi + \frac{1}{2m^*}(-i\hbar\nabla - 2eA)^2 \psi = 0 \hspace{1cm} (32)$$

$$j = \frac{2e}{m^*} Re\{\psi^* (-i\hbar\nabla - 2eA) \psi\} \hspace{1cm} (33)$$

where $j$ represents the dissipation-less electric current density, $Re$ the real part of the wave-function. The first equation determines the order parameter. The second equation then provides the superconducting current.

A compelling piece of evidence for the validity of GL theory was that of flux quantization. Any complex function $\psi$ can be represented as $|\psi|e^{i\phi}$ where $|\psi|$ is the amplitude and $\phi$ is the phase. Changing $\phi$ by $2\pi n$ will not change $\psi$ or any corresponding physical properties. However in a superconductor with non-trivial topology (e.g. that of a superconducting ring), the phase $\phi$ may continuously change from some value $\phi_0$ to $\phi_0 + 2\pi n$ as one travels around the loop to the same initial point. If so, there will be $n$ magnetic flux quanta trapped in the loop. The exact value of this magnetic flux is given by

$$\Phi_0 = \frac{\hbar}{2e} \hspace{1cm} (34)$$

Experimental measurement of the magnetic flux quantum\[8\] gave credence to the concept of describing a superconductor by means of a complex order parameter.

### 1.1.7 Coherence Length and the GL Parameter

One of the most important developments of GL theory was the introduction of a temperature-dependent coherence length

$$\xi = \sqrt{\frac{\hbar^2}{2m|\alpha|}} \hspace{1cm} (35)$$

\[vi\] Again a complete derivation of this is largely outside the scope of this report but further information can be found in Chapter 4 of Tinkham’s *Introduction to Superconductivity*\[8\] (note Tinkham uses CGS units).

\[vii\] A full treatment of this can be found in Chapter 34 of Ashcroft and Mermin’s *Solid State Physics*.\[9\]
where \(\alpha\) is a constant in the Ginzburg-Landau equation for \(\psi\) with the form \(\alpha_0(T - T_c)\). In some limiting cases, it can also be represented by

\[
\xi = \frac{\hbar \nu_f}{\pi \Delta}
\]  
(36)

where \(\nu_f\) is the Fermi velocity and \(\Delta\) is the superconducting energy gap. The coherence length arises from the fact that the superconducting electron density cannot change quickly. It is the minimum length over which a given change can be made, lest it destroy the superconducting state. With this theory, Ginzburg and Landau were able to characterise all superconductors with two length scales; this and the penetration depth.

The ratio of these two lengths defines the GL parameter

\[
\kappa = \frac{\lambda}{\xi}
\]  
(37)

For a typical pure superconductor, \(\lambda \approx 500\,\text{Å}\) and \(\xi \approx 3000\,\text{Å}\), so \(\kappa \ll 1\).

### 1.1.8 Type I and II Superconductors

The introduction of the coherence length lead to an important distinction between two types of superconductors, i.e. those with \(\xi > \lambda\) (type I) and those with \(\xi < \lambda\) (type II). As established, superconducting materials can exist in the normal state or the superconducting state depending on the external magnetic field they experience. However, if we increase the magnetic field to some critical value (which varies from material to material), the Meissner effect will begin to break down. Superconducting materials will experience this effect in one of two ways

1. The superconductor will switch abruptly from zero flux penetration (the superconducting state) to one of complete flux penetration (the normal state) at the critical field \(H_c\). These are known as Type I superconductors.

2. The superconductor will remain in a state of total flux screening (the superconducting state) until a critical field \(H_{c1}\) is reached. At this point, vortices will appear in the material. Where a vortex appears, the order parameter will drop to zero leading to a partial penetration state. After this the superconductor will continuously transition towards full flux penetration (the normal state) at a larger critical field \(H_{c2}\). This is known as a Type II superconductor.
Although we typically expect the flux penetration in a type I superconductor to be abrupt as seen in Fig. 4, this is not always the case when we have a nonzero demagnetizing factor.

When a magnetic field, \( H_a \), is applied to a superconductor, screening currents will appear on the surface of the superconductor and create a demagnetizing field, \( H_D \). We can then relate these two fields to the internal field of the superconductor, \( H_i \)

\[
H_i = H_a - H_D
\]  

(38)

For simplicity, we will only consider the case where the internal field is homogeneous, meaning that the superconductor will have a uniform field inside the body when exposed to a uniform external field. In this case, we express the demagnetizing field as

\[
H_D = nM
\]  

(39)

where \( n \) is the (scalar) demagnetizing factor, and \( M \) is the uniform magnetization of the body.

---

\[viii\] A more complete treatment can be found in Chapter 1.7 of *Superconductivity: Physics and Applications* by K. Fossheim and A. Sudbø.
Applying this to (38)

\[ H_i = H_a - nM \]  

(40)

However, in a superconductor, \( M = -H_i \). Applying that to (40) yields an important relation, as it links the internal field and the applied field

\[ H_i = \frac{1}{1-n} H_a \]  

(41)

We can then rearrange this as

\[ 1 - n = \frac{H_a}{H_i} \]  

(42)

We can expect an intermediate state whenever

\[ 1 - n < \frac{H_a}{H_i} < 1 \]  

(43)

In other words, whenever the demagnetizing factor is nonzero. In a type I superconductor, we can observe an intermediate state, although one that is very different from the intermediate state of type II. Considering materials with \( n \neq 0 \), we can get a better picture of how flux will penetrate in a type I superconductor. The flux penetrates in the form of continuous lamina. The lamina alternate between normal and superconducting layers and are parallel to the field. The thickness of these lamina depends on temperature and the applied field. The superconducting lamina are flux-free while the normal lamina contain a magnetic flux density linked to the critical field, \( B_c = \mu_0 H_c \). In the case of \( n = 0 \), no lamina appear.

In a type II superconductor, the flux penetrates in vortices of magnetic flux quanta and the density of these lines will increase by increasing the applied field. In the case of a type II superconductor, the mixed state is inherent to the material regardless of the value of \( n \). For this reason, type II superconductors are more useful on a large scale, while type I are not.
Figure 5: In (a), the lamina penetrate a type I superconductor when $n \neq 0$ leading to an intermediate state. We can see a more gradual decline to the normal state than the abrupt drop when $n = 0$. In a type II film, we can see that the mixed state will always occur regardless of the value of $n$.

It was against this backdrop that Brian David Josephson produced his groundbreaking theory of superconducting tunnelling in 1962.
1.2 Josephson Junctions

1.2.1 The Josephson Equations

When two superconductors are brought into contact in such a way that the critical current in the contact region, $I_c$, is far lower than that of the individual constituents, that contact is known as a "weak link". Before contact, each superconductor has a wavefunction $\psi$ that is independent and subject to an independent phase $\phi$. As mentioned in 1.1.6, each superconductor wavefunction is characterized by its amplitude and phase, $\psi = |\psi| e^{i\phi}$. Once this weak link is established, coherence is created across the barrier. A phase difference $\Delta \phi$ will cause interference between the formerly independent wavefunctions. When a Cooper pair tunnels from one side of the junction to the other, it probes the phase of both wavefunctions in succession, i.e. the first one with $\phi_1$ and the second one with $\phi_2$. The system can be described as having one wavefunction as a whole.

Josephson predicted in 1962\textsuperscript{19} that such a junction would have entirely unexpected properties. The Josephson effect predicted that a tunnelling effect can be expected for two weakly coupled superconductors, known as a Josephson Junction (JJ), and that such junctions could sustain a tunnelling current even in the absence of a voltage drop, i.e. a supercurrent would form through an insulating barrier.

In the case of two equal superconducting electrodes (i.e. the density of superconducting carriers in both electrodes are equal, $n_{s1} = n_{s2}$), the supercurrent is expressed by the first Josephson equation\textsuperscript{18}

\[ I_s = I_c \sin \varphi \]  

(44)

where $\varphi$, known as the Josephson phase, is the difference in phase across the junction ($\varphi = \phi_1 - \phi_2$), and $I_c$ is a parameter of the junction known as the critical current. This equation is a major result in Josephson Theory as it tells us that the supercurrent is driven across the barrier simply by the superconducting phase difference. As $\varphi$ will remain constant over time, the supercurrent will be a direct current (DC) and take values between $I_c$ and $-I_c$. This is also known simply as the DC Josephson Effect.

The second Josephson equation relates the voltage to the time evolution of the phase difference

\[ \frac{\partial \varphi}{\partial t} = \frac{\Phi_0}{2\pi} V(t) \]  

(45)

This is known as the superconducting phase evolution equation.

\textsuperscript{18}A full treatment can be found in Chapter 5 of Superconductivity: Physics and Applications by K. Fossheim and A. Sudbø\textsuperscript{12}
Equation (45) can be reformulated as

$$\frac{\partial \varphi}{\partial t} = 2\pi [K_J V] = \frac{2\pi}{\Phi_0} V$$  \hspace{1cm} (46)$$

where $K_J$ is known as the Josephson constant and is the inverse of the magnetic flux quantum. If a Josephson junction is irradiated with microwaves of appropriate frequency, the voltage-current characteristics of the junction will be changed in such a way that voltage steps are created that depend entirely on the fundamental constants and the frequency of the microwaves. $K_J$ is the constant of proportionality of the Josephson effect, relating the potential difference across a Josephson junction to the frequency of the irradiation. If we define $\Phi$ as a product of the magnetic flux quantum and the phase,

$$\Phi = \Phi_0 \frac{\phi}{2\pi}$$  \hspace{1cm} (47)$$

then the voltage across the junction can be given by

$$V = \frac{\Phi_0}{2\pi} \frac{\partial \varphi}{\partial t} = \frac{d\Phi}{dt}$$  \hspace{1cm} (48)$$

which is analogous to Faraday’s Law. This voltage does not come from a magnetic field as there is none within a superconductor. This voltage comes from the kinetic energy of the Cooper pairs.

If a fixed DC voltage, $V_{DC}$, is applied across the junction, $\varphi$ will vary linearly with time. In such a case, we get a combination of (44) and (48), known as the weak-link current-phase relation,

$$I(t) = I_c \sin \left( \varphi + \frac{2\pi}{\Phi_0} V(t) \right)$$  \hspace{1cm} (49)$$

where the current is sinusoidal with an amplitude $I_c$ and a frequency $V_{DC} K_J$. This effect is known as the AC Josephson Effect.

1.2.2 Josephson Inductance

If the current and phase are time varying, the voltage drop across the junction will also vary over time. The Josephson relations determine that this behaviour can be modelled by a kinetic inductance named Josephson inductance.

We can rewrite the Josephson Equations as follows:

$$\frac{\partial I}{\partial \varphi} = I_c \cos \varphi$$  \hspace{1cm} (50)$$
\[ \frac{\partial \phi}{\partial t} = \frac{2\pi}{\Phi_0} V \]  

Applying the chain rule, we can express the time derivative of the current

\[ \frac{\partial I}{\partial t} = \frac{\partial I}{\partial \phi} \frac{\partial \phi}{\partial t} = I_c \cos \phi \frac{2\pi}{\Phi_0} V \]  

Using the standard relation for inductance, \( V = L \frac{\partial I}{\partial t} \), we obtain

\[ V = \frac{\Phi_0}{2\pi I_c \cos \phi} \frac{\partial I}{\partial t} = L(\phi) \frac{\partial I}{\partial t} \]  

From this we can extract the kinetic inductance as a function of the Josephson phase

\[ L(\phi) = \frac{\Phi_0}{2\pi I_c} = \frac{L_j}{\cos \phi} \]  

Here \( L_j \) is the characteristic inductance of a Josephson junction, the Josephson Inductance,

\[ L_j = \frac{\Phi_0}{2\pi I_c} \]  

1.2.3 Josephson Energy

Based on the similarity of the Josephson junction to a non-linear inductor, the energy stored in a Josephson junction when a supercurrent flows through it can be calculated.

Assume at some time \( t_1 \), the Josephson phase is \( \phi_1 \); at some time \( t_2 \), the Josephson phase is \( \phi_2 \). The energy increase is equivalent to the work done on the junction.

\[ \Delta E = \int_{t_1}^{t_2} IV \, dt \]  

Substituting Equations (44) and (48) into the above gives us

\[ \Delta E = \int_{1}^{2} I d\Phi = \int_{\phi_1}^{\phi_2} I_c \sin \phi \, d \left( \frac{\Phi_0 \phi}{2\pi} \right) = -\frac{\Phi_0 I_c}{2\pi} \Delta \cos \phi \]  

The crucial result from this is that the change of energy in a Josephson junction is path-independent and depends only on the initial and final state of the junction. Therefore the
energy is a state function and is given by

\[ E(\varphi) = -\frac{\Phi_0 I_c}{2\pi} \cos \varphi \]  

(58)

From this we can extract a characteristic parameter of a Josephson junction, known as the Josephson energy, \( E_J \)

\[ E_J = |E(0)| = \frac{\Phi_0 I_c}{2\pi} \]  

(59)

It is related to the Josephson Inductance by \( E_J = L_J I_c^2 \).

### 1.2.4 Josephson Penetration Depth

Josephson theory also introduces a new length scale to characterize the junctions. The Josephson penetration depth characterizes the typical length on which an externally-applied magnetic field penetrates into a long Josephson junction\[21\]

\[ \lambda_J = \sqrt{\frac{\Phi_0}{2\pi \mu_0 j_c(2\lambda_L + t_{ox})}} \]  

(60)

where \( t_{ox} \) is the thickness of the insulating barrier and \( j_c \) is the critical current density. A long junction is one where one or more of its dimensions is longer than \( \lambda_J \).

### 1.2.5 Weak Link Systems

Although initially greeted with much scepticism, Josephson’s theories were quickly verified the next year, 1963, when Anders and McRowell built the very first JJ\[22\].

A typical realization of a weak link is a superconductor/insulator/superconductor (SIS) tunnel layer junction. This consists of two superconducting films which are separated by a thin oxide layer, typically aluminium oxide, AlO\(_x\). However, there is a remarkable wealth of information on the weak link between two superconductors. For example, in place of a thin oxide layer, a normal (N) metallic layer may be inserted instead to form a SNS junction. In this case, the metal layer can be made thicker. Another method of weak link creation is to create the whole system from a single superconductor, e.g. by splitting a continuous film into two regions, leaving a gap between the two regions of dimensions around \( \xi \). In this case, \( j_c \) is the same in the bridge and the bulk, however the overall critical current of the device is much lower than in the two regions, allowing a weak link. There are also studies that show the weak link can be formed between superconductors and semiconductor nanowires\[23\], superconductors and carbon nanotubes\[24\] and superconductors and graphene\[25\].
1.2.6 Phase Qubits and the Washboard Potential

A quantum bit or qubit is a basic unit of quantum information and can be thought of as the quantum analogue of the classic binary bit\[^{26}\]. A superconducting phase qubit is a solid-state artificial atom composed of JJs, inductors, capacitors and interconnects.\[^{27}\]

If we want to understand how the phase qubit arises we have to consider the Stewart-McCumber Model\[^{28,29}\]. We treat the circuit model of a JJ as a parallel combination of an ideal Josephson junction (that obeys the two Josephson equations) and a resistor (that obeys a generalization of Ohm’s law for nonlinear resistors). The junction typically has a parasitic capacitance, so we introduce a capacitor in parallel with the other two elements to create a resistively shunted capacitor junction (RSCJ) model. By summing the current along the three parallel paths, we get the circuit equation for the junction\[^{30}\]

\[
I = I_c \sin \varphi + \frac{V}{R} + C \frac{dV}{dt}
\]

Utilizing (45), we can reformulate this as

\[
I = I_c \sin \varphi + \frac{\Phi_0}{R} \frac{\partial \varphi}{\partial t} + C \frac{\Phi_0}{2\pi} \frac{\partial^2 \varphi}{\partial t^2}
\]

Bringing the current to one side gives us a dynamic equation for the phase

\[
\frac{\Phi_0}{R} \frac{\partial \varphi}{\partial t} + C \frac{\Phi_0}{2\pi} \frac{\partial^2 \varphi}{\partial t^2} = I - I_c \sin \varphi
\]

The terms on the left hand side are analogous to those of a particle with coordinate (location) \( \varphi \). \( \frac{\partial^2 \varphi}{\partial t^2} \) gives us the particle’s acceleration ergo the mass of the particle is proportional to \( C \). \( \frac{\partial \varphi}{\partial t} \) relates to the particle’s friction which is inversely proportional to \( R \). The particle moves in a conservative forcefield that is given by the expression on the right hand side which corresponds to the particle interacting with a potential energy \( U(\varphi) \) that is given by

\[
U(\varphi) = E_J \left( -\gamma \varphi - \cos \varphi \right)
\]

where \( \gamma = I/I_c \). This is known as the "washboard potential", because it has an overall linear dependence, \( \gamma \varphi \), that is modulated by \( \cos \varphi \), giving it the appearance of a washboard.
The zero voltage state describes one of two distinct behaviours displayed by the phase particle. The mass term will act to reduce the acceleration of a moving body. In this analogy, \( C \) is the mass term. A large \( C \) will reduce the acceleration of the phase. If it is sufficiently large enough, the Cooper pair is stuck in the local minima. Hence the "ball" does not "roll" and no voltage develops as the phase does not change. A Josephson junction will allow currents up to \( I_c \) to pass through without any voltage; this corresponds to the superconducting branch of the Josephson junction’s current–voltage characteristic.

The other behaviour exhibited is the non-zero voltage stage, i.e. \(|I| > I_c\). When a bias is applied, the phase changes and the derivative terms become nonzero. The larger the bias, the larger the phase change which leads to a tilting of the washboard potential. It is analogous to the phase particle free-running down the slope of the potential. This state corresponds to the voltage branch of the current–voltage characteristic. For junctions with large resistance, the zero-voltage and voltage branches will overlap in some range of currents below the critical current, giving a hysteretic behaviour.

The phase qubit operates at the zero voltage state. In a JJ with high resistance and low capacitance, quantum energy levels can be detected in the local minima of the washboard potential at temperatures less than \( 1 \) \( \text{K} \). They were first detected using microwave spectroscopy. A weak microwave signal was added to the bias current and transitions from the zero to the non-zero voltage state were measured across the junction. Resonances were observed at frequencies that corresponded with the quantum transition energies found when solving the Schrödinger equation for the local minimum of the washboard potential. In a classical model, only a single

Figure 6: A plot of the potential energy against the phase, the "location" of the particle.
resonance would be expected, centred at the plasma frequency, \( \omega_p \), the frequency at which electrons oscillate about their equilibrium positions in the absence of a magnetic field. Quantum mechanically, the local minimum of the washboard potential can accommodate several quantized energy levels. The lowest of these (i.e. the transition from ground state to first excited state) is given by \( E_{01} \approx \hbar \omega_p \). However due to the anharmonic nature of the trapping potential minimum, the higher energy transitions (first to second excited state, second to third excited state, etc.) are shifted somewhat below this. The observation of several, discrete energy levels in this fashion gives extremely compelling evidence that a superconducting device behaves quantum mechanically.

An important consequence of the anharmonicity of the washboard potential is that the ground and first excited states can be addressed by a unique frequency without any significant perturbation of the higher excited states. The two lowest states effectively form a two-level system (i.e., a pseudo-"spin-1/2" system). This degree of freedom is used as the qubit.

As they are quantum mechanical objects, they can be coherently controlled, placed into superposition states, exhibit quantum interference effects, and become entangled with one another. The time scale over which a qubit maintains this type of behaviour (and subsequently remains usable for quantum information applications), is known as the "coherence time". Although it might seem straightforward to scale up circuits containing many qubits, this is not the case. In practice, the circuit will couple strongly to many spurious sources of dissipation and dephasing which will lead to decoherence of the qubit state.

### 1.2.7 Two Level System defects and their effect on coherence

In the context of superconducting qubits, a two level system (TLS) defect is a localized low-energy excitation that is predominantly found in non-crystalline dielectric materials, such as those used to form the insulating layer of a JJ. The microscopic nature of a TLS defect is unclear. It has been postulated that they result from an oxygen atom or vacancy, arising from the oxide barrier layer, that could sit in a double-well potential and tunnel between two positions. It has also been theorized that a quasiparticle hopping between two positions in the oxide barrier layer could give rise to them. Regardless, on an atomistic level, a TLS defect can be viewed as an ion or electron that can tunnel between two spatial quantum states. These will arise due to defects in the crystal structure or the presence of polar impurities such as OH⁻.

The extent to which TLS defects affected the coherence of qubits was not fully understood until 2004 when Simmonds et al. observed spurious microwave resonators in a phase qubit. In this seminal work, Simmonds and his team investigated the Rabi oscillations of a qubit. These Rabi oscillations occur when light is incident on a TLS defect leading to a periodic
exchange of energy between the light field and the TLS defect. They measured the Rabi oscillations between the ground and first excited states by irradiating the qubit with microwaves at a frequency of around $5 - 10 \, \text{GHz}$ and then measuring the probability of the qubit being in the first excited state. They were able to show that these resonators limited the coherence of the qubit by severely degrading the coherence of the Rabi oscillations. Simmonds argued that these resonators arise from two-level states within the tunnel barrier, which couple to the qubit’s states through the critical current. They are also believed to lead to energy level splitting. This was a major advancement in the field as it uncovered a previously unknown term in the Hamiltonian of a Josephson junction that had gone unnoticed since its discovery.

Building from this, Cooper et al. were able to demonstrate quantum-coherent oscillations between a qubit and TLS defect. From their results, they found that the coherence time of a TLS defect can be at least as long (if not longer) of that of a qubit. Once the TLS defect absorbs the qubit energy after 10 ns, it doesn’t immediately decay from the first excited state to the ground state. The time span of the decay is about 1 to 2 times the coherence time of the qubit.

There are two ways in which a TLS defect in a tunnel barrier can interact with the qubit. In the first scenario, the dipole moment of the TLS defect couples directly to the voltage across the junction. When the TLS defect and the qubit are in resonance, charge fluctuations in the TLS defect drive phase oscillations in the qubit leading to the two systems becoming coupled. The qubit exchanges energy with the TLS defect which loses that energy via phonon emission, resulting in decoherence. In the second scenario, low-frequency charge fluctuations in the TLS defect cause the height of the junction’s tunnelling barrier to fluctuate. This leads to critical current noise which produces fluctuations in the energy level splitting of the qubit and leads to decoherence.

1.2.8 Revisions to Josephson Junction Design

Despite uncertainty in their exact cause, it is an immutable fact that their presence is due to the thin oxide layer present in all SIS junctions. To reduce the impact of TLS defects on coherence time, many researchers attempted to revise and optimize the design.

In general, the amorphous AlO$_x$ insulating barrier is formed by oxidising the surface of a thin layer of Al that separates the superconducting electrodes. AlO$_x$ is a popular choice of insulating layer for various reasons, chiefly that it reliably works as an barrier layer at thickness of around 1-2nm. However, below this thickness AlO$_x$ fails to provide a reliable barrier as defects begin to appear. This limits the development of high critical current density junctions.

In 2006, Oh et al. demonstrated that the number density of TLSs in the insulating oxide could
be drastically reduced by improving the quality of the oxide. Oh and his team fabricated the first high quality JJ with a crystalline oxide layer. Fabricating the device from a trilayer grown on a single-crystal Al₂O₃ (0001) substrate, the layers consisted of a base Rhenium (Re) layer (chosen for its low free energy of oxidation and good lattice match with sapphire), a single crystal Al₂O₃ tunnel layer, and a polycrystalline Al top layer. An ~ 80% reduction in the density of TLSs was reported.

However, little progress has been made beyond this reduction in the density of defects. The preferred approach taken by the community to avoid TLSs, which are primarily seen in phase qubits (1-10 \( \mu m \)), is to build qubit designs with smaller dimensions (0.1-0.3 \( \mu m \)) to reduce the net number of defects. In contemporary qubit design, it is speculated that TLS defect density may decrease due to the reduced effects of stress in smaller geometries with some reports demonstrating small junctions that exhibit low-loss junction inductance and junction capacitance.

Regardless, in terms of long term scalability, the issue of the tunnel barrier should not be ignored. When scaled to hundreds or thousands of junctions and targeting a high yield with minimal variation between junctions, it is clear that defect density will impact performance and further work on JJ architecture is warranted.

1.2.9 Vicinal Surfaces

As outlined in Sections 1.2.7 and 1.2.8, the use of an amorphous AlOₓ barrier layer gives rise to TLS defects that greatly affect the coherence time of the superconducting phase qubit and the thickness limit of 1-2 nm hinders the development of high current density JJs. For this investigation, a novel architecture that removes the need for an amorphous barrier layer was investigated.

This novel approach to redesigning the JJ architecture is predicated on the use of a stepped, or vicinal, surface as the weak link between superconducting electrodes. This is based on recent advances in surface science, and in particular on the methodology for the formation of regular stepped surfaces and the growth of films on such surfaces, coordinated with the terraced substrate morphology. These advancements are a speciality of the Applied Physics Research Group (APRG).

Consider a surface misaligned from a low Miller-index plane by a small angle of 0.5-5°. If this plane were subjected to a thermal anneal, it may rearrange itself in the form of a regular pattern of atomic terraces separated by single atomic steps. These terraces are virtually defect-free as all vacancies and adatoms that form point defects will migrate along the surface until they attach to upper or lower atomic steps running along the terrace.
The vertical separation between adjacent atomic terraces is perfectly identical across large areas of the surface, even though such an area could be 100 \( \mu m \) in scale. For single atom height steps, the separation between adjacent atomic terraces is equal to the separation \( d \) between atomic planes with Miller indices (100). The width of these atomic terraces can easily be controlled by altering the miscut angle \( \theta \). This is described by the function

\[
w = \frac{d}{\tan \theta}
\]  

(65)

In order to increase the width of the terraces, only the value of \( \theta \) needs to be reduced. By changing the conditions of the annealing and by changing \( \theta \), it is possible to change the step height from a single atomic step to double or multiple steps. The process of a surface decomposing into two or more planar surfaces is known as "faceting". It is even possible to create trains of single steps known as "step bunches" which are separated by perfectly flat atomic terraces of large width.\footnote{Previous studies have investigated the surface evolution of sapphire as a function of several annealing parameters. Variations in temperature of the anneal, time spent annealing, the miscut angle of the substrate used for the anneal, and the pressure the anneal is performed under are all considered in optimizing the faceting process.} Annealing vicinal c-plane Al\(_2\)O\(_3\) substrates in air at 1000 - 1500\(^\circ\)C for several hours can create a step-and-terrace morphology with terraces that are several hundreds of \( nm \) wide separated by steps, 1-5\( nm \) high.\footnote{Growth of nanostructures on these surfaces would require deposition of the material on the substrate in the form of a collimated beam with careful control over the angle between the mean plane of the surface and the direction of the beam. This technique is known as "Atomic Terrace Low-Angle Shadowing" or ATLAS and will be discussed in the next chapter.}

1.2.10 Stepped Weak Link Josephson Junctions

There are three novel junction architectures to be explored in this study. The first one is that of the \textit{Multiterrace Junction} (MTJ) as shown in Fig. \footnote{The MTJ consists of two superconducting layers deposited on two adjacent terraces. The separation between the terraces can be controlled in a range from 0.2 – 20\( nm \). A consequence of this approach is that it is not material specific. In theory, it should be possible to form a dielectric barrier of any material such as Si\(^{28}\) or Si\(^{29}\), two common isotopes of Si important to the study of qubits due to their zero nuclear spin.}.

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As seen in Fig. 7, structures known as "anti-steps" or "anti-bands" are elevations at terraces near the step-down locations. These are a result of the dependency of the step migration velocity on the terrace width and can be created by direct current heating with high current density. The benefit of these antibands is that they allow for additional control of the separation between superconducting electrodes on the adjacent terraces. One could increase the separation between electrodes and use electrodes of greater thickness. This is beneficial as the electrode thickness should be comparable to the coherence length $\xi$. If the thickness is less than the coherence length, the critical temperature of the junction is reduced and will require cooling at a lower temperature in order to transition to the superconducting state. Therefore, increasing electrode thickness would raise the critical current and make for a more robust JJ.

The second architecture to be investigated is the Atomic Terrace Shadowed Gap (ATSG) junction as seen in Fig. 8.

In this architecture, the flux of superconducting metal needs to be collimated and should be
directed at the surface at an angle close to but less than normal, with respect to the surface of a terrace along the descending step direction. Gaps are formed along the inner sides of the step edges between superconducting layers on adjacent terraces. These gaps could be as small as $0.2 - 0.5\,\text{nm}$ in width.

The last of these architectures is Atomic Scale Constriction in a Wire (ASCW). This is based on utilising a superconducting film deposited on a single flat atomic terrace such that there is a constriction along the terrace due to a kink along the edge of the atomic step.

![Figure 9: A terrace of Strontium titanate (SrTiO$_2$) (001) where the atomic constriction is highlighted in green. Adapted from Toktarbaiuly (2015).](image)

It is possible to have constrictions on the terraces with widths of $0 - 1\,\text{nm}$, down to the width of less than an atom. Areas of superconducting film posited on the same terrace and separated by a gap of $0 - 2\,\text{nm}$ wide can also be identified. This gap is the result of the step edge kink. The thickness of the superconducting film across the entire terrace remains the same. An example of this morphology can be seen in Fig. 9. Although this is SrTiO$_2$ (001), similar morphologies can be obtained in other materials provided the angle of the miscut and the annealing conditions are optimized.

1.2.11 Al$_2$O$_3$ as a substrate

$\alpha$-Al$_2$O$_3$, more commonly known as sapphire, is a single crystal form of the alpha phase of the mineral corundum. It sees a wide variety of uses given its unique combination of mechanical, optical, and radiation properties. It is chemically stable and electrically insulating but has good thermal conductivity. It crystallizes in a hexagonal structure with a rhombohedral primitive cell as seen in Fig. 10. In the hexagonal unit cell, the lattice vectors of the basal plane are equivalent ($a_1 = a_2 = a_3 = 4.758\,\text{Å}$) and are separated by an angle of $120^\circ$. The lattice vector $c$ has a length of $12.992\,\text{Å}$. The $O^{2-}$ anions form a distorted hexagonal close-packed lattice, with the $Al^{3+}$ cations filling two-thirds of the octahedral hollows. The strong
Oxygen bonding lends the material its hardness and insulating properties.

Figure 10: Figure (a) produced with VESTA

The most commonly encountered planes are seen in Fig. 10b. c-plane (0001) Al₂O₃ is one of the most commonly used substrates as it has a low surface energy making it a very stable surface. It is preferable for this work due to its ability to form ordered steps on its surface. There are three different possible terminations on the (0001) plane. Each termination exposes a different surface crystal structure; an oxygen layer, a double aluminium layer, or a single aluminium layer. This last layer is the most favourable as it has the lowest surface energy of all three.
2 Experimental Methods

2.1 Fabrication Methods

2.1.1 Atomic Terrace Low Angle Shadowing

Atomic Terrace Low-Angle Shadowing (ATLAS) is a technique which enables growth of planar nanowire or nanodot arrays using molecular beam epitaxy (MBE) on a vicinal surface. The atomic step-and-terrace morphology of vicinal substrates can be utilized to produce a shadowing effect on a highly collimated molecular beam which is at an oblique angle to the substrate. The collimation of this beam is achieved by placing the evaporation source at a large working distance (between 40-100 cm) from the substrate.

As mentioned, a key component of this technique is an epitaxial process where materials are grown on heated substrates by the interaction of adsorbed species supplied by atomic or molecular beams. It takes place under ultra high vacuum (UHV) \(10^{-8} - 10^{-11}\) mbar conditions. The deposited layers can have the same crystalline structure of the substrate and a lattice parameter that differs by no more than 10% of that of the substrate. The molecular beams are created by the evaporation of suitable materials contained in ultra-pure crucibles. Control of the heat required to evaporate the source materials will control the rate of material that impinges on the substrate surface.

Two important requirements of MBE, as stated above, are a heated substrate and UHV conditions. The temperature of the substrate will affect the rate of desorption and the diffusion rate of species on the substrate which are necessary for the formation of an ordered lattice. UHV conditions are necessary so as to reduce the incorporation of impurities in the growth environment, in turn producing high-purity surfaces.

According to the kinetic theory of gases, the amount of a species \(i\) can be found using

\[
N_i = p_i \left( \frac{N_A}{2\pi M_i k_B T} \right)^{1/2}
\]  

where \(p_i\) is the partial pressure of the species, \(M_i\) is the molecular weight, \(k_B\) is the Boltzmann constant, and \(N_A\) is Avogadro’s constant. In a growth of something like Gallium Arsenide (GaAs), a typical contaminant is C, which arises from the presence of CO, a common vacuum background species. When growing GaAs at rates of a monolayer (ML) per second, the required partial pressure of CO to minimise C contamination is \(p_{CO} \approx 2 \times 10^{-12}\) mbar, a
value which gives justification to the requirement of UHV conditions.

A useful consequence of the necessity of UHV conditions is that MBE growth takes place in the molecular regime. The molecular regime is characterised by mean free paths larger or comparable to the distance between the crucible and the substrate. In this regime, atoms and molecules are more likely to collide with the substrate (or walls of chamber) before colliding with another gas molecule and mechanical beam shutters can be used to block the beams directed at the substrate. The composition of the material can be abruptly changed in times given by the actuation times of the shutters, on the order of 0.1s. Since the MBE growth rate can be in the order of $ML/s$, the thickness of the interfaces between layers of different composition can be in the order of tenths of a $ML$.

To confirm that MBE growth takes place in the molecular regime, we recall that according to the kinetic theory of gases, the mean free path $\lambda_{MF}$ between collisions of atoms or molecules at a pressure $p$ is given by

$$\lambda_{MF} = \frac{k_B T}{\sqrt{2\pi p D^2}}$$

where $D$ is the diameter of atoms or molecules in the beam. Therefore, for MBE operating pressures of $10^{-6} - 10^{-4}$ mbar, we will get $\lambda_{MF} = 5 - 0.05m$ respectively. Hence the atoms and molecules will have practically collision free paths towards the substrates, confirming molecular growth.

The deposition system used in this study is a 200 mm diameter stainless steel UHV chamber equipped with a fast-entry loadlock as seen in Fig 11. The typical base pressure that can be achieved with this system is $3 \times 10^{-10}$ mbar by use of a turbomolecular pump. The primary source is a Telemark Model 568 UHV Multi-Pocket Electron Beam Evaporator. The electron beam (E-beam) gun consists of an electron-emitting filament and a crucible containing the...
evaporation material. The filament is located directly beneath the crucible. As the electrons are emitted, a potential of $6kV$ is applied between crucible and filament to accelerate the electrons while a magnet deflects the e-beam onto the crucible. The 568 evaporator is equipped with six 7cc crucibles and a quartz crystal monitor to record the rate of deposition of each species during evaporation. The working distance between the evaporator and the substrate is 370 mm.

![Sample Plate](image)

**Figure 12:** Sample Plate. A Ta mask is placed over the substrate and screws are attached to the four rods at each corner to hold the substrate in place.

The substrate is mounted onto a stainless steel sample plate, covered by a tantalum mask, and secured in place with 4 screws as seen in Fig. [13]. The sample stage is machined to accept the sample plate. The sample plate is transferred and docked into the sample holder by means of a spring-loaded transfer fork at the end of a magnetic linear drive. The sample stage contains a tungsten filament which resides 2-3mm below the sample plate position, the purpose of which is to heat the substrate surface during deposition in order to ensure the growth of crystalline films.
2.1.2 DC Magnetron Sputtering

DC Magnetron Sputtering is a physical vapour deposition (PVD) method of thin film deposition by sputtering, a phenomenon in which microscopic particles of a solid material are ejected from its surface, after the material is itself bombarded by energetic particles of a plasma or gas. Atoms liberated by the sputtering process create a flux of sputtered material forming a vapour cloud. The vapour cloud then deposits a thin film coating on the substrate surface.

![Diagram of magnetron sputtering process](image)

**Figure 13:** Schematic of the magnetron sputtering process. Ar atoms bombard the sputtering target liberating electrons which then deposit on the substrate surface.

During the process, the chamber is evacuated to high vacuum (HV) pressures ($10^{-5}$ mbar) to remove impurities such as H$_2$O, H$_2$ and Ar. It is then backfilled with a high-purity process gas, commonly Ar owing to its large atomic mass, inert chemistry, and relatively low cost. Typical sputtering pressures can range from $10^{-4} - 10^{-2}$ mbar.

A high negative voltage (-0.5 to -5 kV) is applied to the target surface so it can act as a cathode. The substrate will thus act as an anode. The neutral Ar atoms will collide with the negatively charged target and become ionized. They are then ejected into high-density plasma as a result of neutralization. The gas ions will remain in the vacuum and liberate the target atoms. The liberated atoms are driven to the substrate where the positive ions condense and form a thin film coating on the surface. DC Magnetron sputtering uses magnets behind the negative cathode to trap electrons over the negatively charged target material so they are not free to bombard the substrate, allowing for faster deposition rates. Compared to other methods such as MBE, DC magnetron sputtering is a relatively simple technique with a high deposition rate. This allows manufacturers to fabricate thin films quickly, economically and efficiently.
2.1.3 Annealing Set Up

Figure 14: Fig. 14b gives a side view of the furnace. The alumina tube that runs through the centre of the furnace is plugged at either end with an alumina stopper. This prevents heat from leaking out. Minimizing heat leakages reduces the amount of power required to maintain the unit at the desired temperature.

The high temperature furnace used for all annealing in this study is an MTI Corporation GLS-1600X. It contains 4 silicon carbide (SiC) heating elements that generate heat via the principle of the Joule effect, \( P \propto I^2 R \). An alumina tube is used to load samples into the furnace and is placed along the centre of the heating elements. The maximum working temperature of the system is 1550°C ± 5°C. It has a maximum heating rate of 10°C/min. There is a total heating zone length of 390 mm with a constant temperature zone of 160 mm at the centre of the tube (±1°C). A PID controller is used to select the desired temperature with an accuracy of ±1°C.

2.1.4 Reactive Ion Etching

Reactive Ion Etching (RIE) is a type of dry etching technology where chemically reactive plasma is used to remove material deposited on wafers. Inductively coupled plasma (ICP) is a type of plasma source produced by electromagnetic induction. An ICP-RIE system (commonly referred to as an ICP etcher) is a system that uses the principles of ICP-RIE to etch material.

A typical ICP etcher consists of a cylindrical vacuum chamber with an electrically isolated wafer platter at the bottom of the chamber. Gas is introduced to the chamber through small inlets in the top of the chamber and exits the chamber at the bottom into the vacuum pump. Plasma is produced in the system by applying a strong radio frequency electromagnetic field to the wafer platter. The oscillating field strips the gas molecules of electrons, ionizing them
and creating a plasma.

The electrons are accelerated up and down the chamber sometimes striking the chamber walls or the wafer platter. The electrons that strike the walls are absorbed and fed out to ground and do not affect the electronic state of the system. Those that are deposited on the wafer platter cause the platter to build up charge due to its isolation. The charge build up develops a large negative voltage on the platter, on the order of a few hundred volts. The plasma itself will also develop a slightly positive charge due to the higher concentration of positive ions compared to free electrons.

The large voltage difference will call these positive ions to move towards the wafer platter where they collide with the sample to be etched. The ions will reactchemically with the materials on the surface of the samples but can also sputter some of the material by transferral of kinetic energy.

The ICP Etcher used in this study was an Oxford Instruments Plasmalab System 100. The etcher consists of a load lock system with a 200 \textit{mm} lower electrode, a 3kW ICP source, a 600W RF RIE bias power, and a helium backside cooling with mechanical clamp.

Figure 15: Oxford Instruments Plasmalab System 100 in Trinity College Dublin’s Cleanroom.
2.2 Characterisation Methods

2.2.1 X-Ray Diffraction

X-ray diffraction is a technique used to study the crystalline structure of materials. When a propagating x-ray wave encounters some regularly spaced particles, diffraction will always occur. X-rays are high energy electromagnetic waves with short wavelengths, on the order of the atomic spacing of solids. Atoms will scatter x-ray waves primarily through their electrons but also through secondary spherical waves emanating from the electrons. This is known as elastic scattering. Since a crystal is a regular array of atoms, it can effectively be considered a regular array of scatterers. This regular array of scatterers produces a regular array of spherical waves.

The phase of the diffracted waves influences the resulting interference pattern. Not all diffracted waves will appear due to destructive interference which results from the overlap of out of phase waves. Some will add constructively in a few directions and are determined by Bragg’s Law.

![Figure 16: Bragg Diffraction](image)

Assume we have a crystal with parallel planes A and B as shown in Fig. 16. The inter-plane spacing is given by \( d_{hkl} \), where \( h, k, l \) are the Miller indices. A beam of X-rays with wavelength...
\( \lambda \) hits these planes at an angle \( \theta \). Two waves are scattered by atoms \( P \) and \( Q \) at the same angle \( \theta \). When the diffracted waves have the same phase, constructive interference will occur. The path difference between wave 1 + 1’ and 2 + 2’ should be exactly equal to an integer multiple of the wavelength. The path difference \( |SQ| + |QT| \) is given by \( 2d_{hkl} \sin \theta \). Thus, Bragg’s Law for constructive interference tells us

\[
n \lambda = 2d_{hkl} \sin \theta \tag{68}
\]

The X-Ray Diffractometer used throughout this study is a Bruker D8 Advance XRD. It has an x-ray tube with a Cu anode, a Göbel mirror to convert the output of the tube into a parallel beam and a 2 bounce monochromator to select the Cu K\( \alpha \) emission from the spectrum (\( \lambda = 1.54\AA \)).

### 2.2.2 X-Ray Reflectivity

X-ray reflectivity (XRR) is a technique to characterize surfaces, thin films and multilayers. This technique allows the determination of the thickness, roughness and density of films. The interaction of an x-ray with matter can be well described by an the refractive index, \( n \), which characterizes the change of direction of the x-ray when passing from one medium to another. In the x-ray regime \( n \) is given by

\[
n = 1 - \delta - i\beta \tag{69}
\]

where \( \delta \) accounts for dispersion and \( \beta \) for absorption.

If an x-ray of wavelength \( \lambda \) is incident on a flat sample, we consider the refractive index of the medium above the sample (generally air) to be 1. For x-rays, the refractive index of a material is slightly less than unity. Passing from air (\( n = 1 \)) to the material (\( n < 1 \)), the possibility of total external reflection arises. In the case of an incidence angle \( \theta_i \) smaller than the critical angle \( \theta_c \), total external reflection will take place and it can be shown that

\[
\sin \theta_c = \sqrt{2\delta} \tag{70}
\]

A consequence of this is that below \( \theta_c \), a material will behave as a perfect reflector of incident x-rays. The position of the critical angle can be directly related to the refractive index which in turn can be used to calculate the density.

The interference fringes on a reflectivity curve can provide information on the thickness, \( t \), of a thin film. The angles of the maxima and minima of the interference fringes are related
to $t$ by the modified Bragg Equation\(^{67}\)

$$\sin^2(\theta_i) = \theta_c^2 + \frac{(m_i + \Delta m)^2 \lambda^2}{4t^2} \quad (71)$$

where $m_i$ is an integer number of the fringe and $\Delta m = 1/2$ or 0 for the maximum and minimum of the fringe respectively.

Although crystalline structures were the primary focus of this study, it is important to note that XRR is not only sensitive to crystalline surfaces. The intensity of the reflected x-ray is related to the average electron density.\(^{68}\) Thus the study of single crystal, polycrystalline and amorphous materials is possible with XRR.

### 2.2.3 X-Ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) is a powerful surface sensitive analytical technique. In it, x-rays are incident the surface of the sample to liberate electrons and the kinetic energy of the electrons emitted is measured. The two characteristics of XPS that make it a powerful technique are its surface sensitivity and its ability to reveal chemical state information about the elements in the sample.

It is based on the Photoelectric Effect, first formally explained by Albert Einstein in 1905.\(^\text{69}\) The use of photoemission as an analysis method was presented by Steinhardt and Serfass in 1951,\(^\text{70}\) however the bulk of work in developing XPS was done by Kai Siegbahn at the University of Uppsala in Sweden in the 1950s and 1960s.\(^\text{71,72}\)

During XPS, the sample is irradiated with x-rays. The most common photoemission x-ray sources use a thoriated tungsten filament that emits electrons, accelerated by a high voltage in a range of 10-15 kV, which are directed to an anode. By bombarding the anode with high kinetic energy electrons, x-ray line emission occurs. The emitted x-rays can be monochromated by quartz crystals that “select” the $K\alpha$ line of Al ($1486.7\text{eV}$). The kinetic energy ($KE$) of the remaining electrons emitted from the anode is measured. Although ($KE$) is the quantity that is recorded by XPS, the derived binding energy ($BE$) is typically used to show the energy spectrum. $KE$, $BE$ and $h\nu$ are related by the following expression

$$KE = h\nu - (\Phi_{\text{sample}} + BE) \quad (72)$$

The binding energy is a measured with respect to the Fermi level of the sample and hence an additional term must be introduced, the sample work function, $\Phi_{\text{sample}}$. These quantities are either known ($h\nu$, $\Phi_{\text{sample}}$) or measurable ($KE$), so it is a trivial matter to rearrange (72) to find the electron binding energy. The binding energy of an electron is a material dependent
property and is independent of the x-ray source used. However the kinetic energy will vary with x-ray source.

When the XPS core electron is emitted, it leads to a core "hole". An electron from a valance orbital will fill this hole in order to reduce energy. This process releases energy in one of two ways; x-ray fluorescence\(^1\) or the emission of an Auger electron. Auger electrons can be detected and this process is the basis of Auger spectroscopy.

As mentioned, XPS is a surface sensitive technique\(^2\) The x-rays can penetrate relatively deeply into the material, usually a few \(\mu m\)\(^3\). Electrons generated at this depth will experience many inelastic collisions and will generally lose their energy before escaping the sample and reaching the detector. Electrons generated closer to the surface are statistically less likely to experience inelastic collisions but will reach the detector with less kinetic energy than elastically scattered electrons. These electrons contribute to the vertical step in the background signal of a large photoelectron or Auger electron emission. Only the electrons from the surface region will lose no kinetic energy by the time they reach the detector. It is these electrons that will contribute to the characteristic photoelectron peaks.

The surface sensitivity of XPS originates from the finite inelastic mean free path (IMFP) an electron has within a solid before undergoing energy losses\(^5\). The intensity of the electrons emitted from a sample at some depth \(d\) is given by Beer’s Law\(^6\)

\[
I = I_0 e^{-d/\lambda_{AL}}
\]

(73)

where \(I_0\) represents the total number of electrons generated from the sample and \(\lambda_{AL}\) is the attenuation length of the electron that is affected by the electron’s energy and the material in which it travels. The attenuation length is similar to the IMFP but it also takes into account the effect of elastic scattering. Electrons with KE of \(\sim 1keV\) will have an IMFP on the order of a few nm. From (73), it can be shown that around 95\% of these electrons will escape from a depth of around 10nm. This depth of 10nm is often called the sampling depth and is defined as the maximum depth normal to the surface from which useful information about the sample can be obtained\(^7\). The higher the energy of the x-ray source, the greater the IMFP of the electrons, and therefore the greater the depths from which the electrons can escape.

\(^{1}\)This is not detected in the electron spectrum and hence is superfluous to this study.
In the course of this study, XPS measurements were carried out on an Omicron Multiprobe XPS system. The system consists of three main chambers; a load lock for sample loading, a preparation chamber for low energy sputter cleaning and high temperature annealing of samples, and an analysis chamber containing a dual filament x-ray source with an Al anode, a quartz crystal monochromator, and a hemispherical electron energy analyser for XPS. The sample, along with the x-ray source and monochromator, are positioned on a Rowland circle of 500 mm diameter. The Rowland circle is a circle of radius \( R \) that lies tangent to a concave curved diffraction grating of radius \( 2R \). The x-ray wavelengths are monochromated in such a way to separate the wavelengths by diffraction angle. This allows for selection of the \( K_\alpha \) line at 1486.67 eV via the design of the chamber geometry.

### 2.2.4 Low-energy Electron Diffraction

Low-energy electron diffraction (LEED) is a technique for the determination of the surface structure of crystalline materials via irradiation of a surface with a collimated beam of low-energy electrons (30-200 eV) and observation of a diffraction pattern of elastically backscattered electrons on a fluorescent screen.\(^7\) It was first discovered in 1927 by Davisson and Germer who fired low-energy electrons at a crystalline nickel target and observed an angular dependence on the intensity of backscattered electrons.\(^7\) This was one of the first experiments to verify the wave nature of electrons. Although developed in 1927, the high surface sensitivity of the technique meant it did not see development as an analytical method until the 1960s when ultra high vacuum systems became more widely available and better methods of surface preparation were developed.
The three main components of a LEED system are visualised in Fig. 18 and are as follows:

1. An electron gun which accelerates monochromatic electrons via a cathode filament at a negative potential, \(-V\), with respect to the sample. A series of electrodes act as "lens" to focus the electrons into a beam of \(\sim 0.1\text{ mm}\) diameter. Some of the electrons that are incident on the surface will be backscattered elastically. Diffraction can be detected provided there is sufficient order on the surface.

2. A high-pass filter in the form of a retarding field analyser. This will filter out everything except elastically scattered electrons. The filter generally contains four hemispherical concentric grids. As only radial fields around the sample are permitted through the filter and the geometry of the sample and surrounding area is not spherical, the space between the sample and analyser must be field-free. The first and fourth grids are held at ground to ensure the elimination of stray fields. A potential difference of \(-V \pm \delta V\) is generated between the second and third grids to prevent inelastically scattered electrons from reaching the screen.

3. A hemispherical, fluorescent screen which is used to observe the diffraction pattern. It is at a positive bias to accelerate the elastically scattered electrons towards it.

Figure 18: A schematic of the three main components of a LEED system.

The LEED obtained in the course of this study were from the LEED apparatus in the Omicron Multiprobe XPS system. In addition to sputtering and annealing facilities, the preparation chamber also contains a fluorescent screen to facilitate LEED measurements.
2.2.5 Atomic Force Microscopy

Atomic Force Microscopy (AFM) is a type of scanning probe microscopy developed in 1986 by Binnig et al.\cite{81} following their work in developing the parent probe, the Scanning Tunnelling Microscope (STM). It is a high-resolution technique with resolution on the order of fractions of a nanometer.

![Figure 19: Schematic of an AFM.](image)

As seen in Fig. 19, an AFM uses a cantilever with a very sharp tip to scan over a surface. As the tip approaches the surface, the attractive force between tip and surface causes the cantilever to deflect towards the surface. At short tip-surface distances, the repulsive force dominates and causes the cantilever to deflect away from the surface. A laser beam is reflected off the top of the cantilever and any deflections towards or away from the surface are recorded by a position-sensitive photo diode (PSPD). By using a feedback loop to control the sample height, constant laser position can be maintained. Thus, an AFM can generate an accurate topographic map of the surface features.

AFM is particularly useful in that it can be applied to variety of surfaces be they a conductor, insulator or semiconductors. This has advantages over standard STM which cannot analyse non-conductive surfaces because it works on the concept of quantum tunnelling and thus
requires the sample to be conducting in order to apply a bias voltage between sample and tip and produce a tunnelling current.

The Atomic Force Microscope utilized in this study is an Asylum MFP-3D AFM. AFM has three primary modes of operation:

**Contact Mode:** In contact mode, the tip is dragged across the surface of the sample. The contours of the surface are measured using the deflection of the cantilever or the feedback signal required to keep the cantilever at a constant deflection. To minimise noise and drift, cantilevers with a low spring constant \( k < 1 \text{ N/m} \), i.e. low stiffness cantilevers, are used to achieve a large enough deflection signal while keeping the interaction force low.\(^8\)

**Non-contact Mode:** In non-contact mode, the tip does not make contact with the sample surface. By using a highly stiff cantilever and monitoring the change in oscillation imposed by the attractive force in this regime, it is possible to maintain the cantilever very close to the surface without transitioning to the repulsive regime. In this regime, changes in the cantilever’s resonant frequency, caused by the attractive van der Waals forces of the surface acting on the tip, can cause changes in the oscillation amplitude and frequency. The change in amplitude or the change in phase can be used in the feedback circuit to maintain the tip at a fixed distance from the surface. Measuring the tip to sample distance at each \((x,y)\) coordinate allows for a topographic image of the surface to be constructed.\(^8\)

**Intermittent Contact Mode:** In ambient conditions, most samples will develop a liquid meniscus layer. If contact mode is attempted in ambient conditions, it will lead to a problem with preventing the tip from sticking to the surface. In intermittent contact mode (or tapping) mode, the cantilever is oscillated at or near its resonance frequency which can be achieved utilizing a piezo element in the cantilever holder. By keeping the frequency and amplitude of the driving signal constant, the amplitude of the cantilever oscillation will also be kept constant. The interaction of forces acting on the cantilever when the tip approaches the surface, including (but not limited to) van der Waals forces, dipole-dipole interactions and electrostatic forces, cause the amplitude of the cantilever’s oscillation to change as the tip gets closer to the sample. The height of the cantilever is adjusted to maintain the oscillation amplitude. The AFM image is produced by imaging the force of the intermittent contacts of the tip with the sample surface.\(^8\)

Intermittent contact mode was used for all scans presented in this report.
2.2.6 Cryocooler

For thermal measurements undertaken in this research study, a Sumitomo RDK-101D Cryocooler was used in conjunction with a Zephyr HC-4A Compressor. The Cryocooler utilizes helium as its refrigerant. It can achieve a minimum temperature of $\sim 3K$ and has a cooldown time to 4.2K of approximately 150 minutes. It operates under the Gifford-McMahon (GM) cycle.[5]

![Figure 20: Schematic of a GM cryocooler. $V_l$ and $V_h$ are buffer volumes of the compressor. The compression heat is removed by the cooling water of the compressor via a heat exchanger. The rotary valves alternate to connect the cooler to the high and low pressure sides of the compressor and run concurrently with the displacer. Image ©Adwaiele/Wikimedia Commons/CC-BY-SA-3.0](image)

A schematic of a GM cryocooler is seen in Fig. 20. In a GM cycle cryopump, helium, kept at pressures around 10-30 bars, is used as the working fluid. The cold head contains a compression and expansion space, a regenerator, and a displacer.

![Figure 21: The four stages of cooling in a GM cryocooler. Image ©Adwaiele/Wikimedia Commons/CC-BY-SA-3.0](image)
In Fig. 21, we can see the process under which a GM cryocooler operates. The cycle starts with the low pressure (lp) valve closed, the high pressure (hp) valve open and the displacer all the way to the right in the cold region. All gas is at room temperature.

- **a to b:** The displacer moves to the left while the cold head is connected to the hp side of the compressor. The gas passes through the regenerator cooling it from an ambient temperature $T_a$ to $T_L$. This causes the pressure to decrease and further gas is able to enter the system to maintain the maximum cycle pressure.

- **b to c:** The hp valve is closed and the lp valve is opened. Fluid escapes causing the pressure to decrease. The decrease in pressure causes a reduction in the gas temperature. This is the useful refrigeration part of the cycle.

- **c to d:** The displacer moves to the right while the cold head is connected to the lp side of the compressor thus forcing the cold gas to pass the regenerator. The gas will take up heat from the regenerator.

- **d to a:** The lp valve is then closed and the hp valve opened. The gas in the hot end of the cold head is compressed and released to the surroundings returning us back to position a.

### 2.2.7 Four Point Probe Measurement

The aforementioned cryocooler is used in conjunction with a four point probe measurement system to measure the sheet resistance of the thin films as the temperature approaches the superconducting regime. A four point probe consists of four electrical probes in a line with a spacing between each of the probes. It operates by applying a current on the outer two probes and measuring the voltage drop between the two inner probes.

The primary advantage of using a four point probe to perform electrical characterisation is the elimination of contact and wire resistances from the measurement. A diagram of the circuit resistances can be seen in Fig. 22. The applied current, $I$, enters and leaves the sample via the outer probes. No current flows through the two inner probes due to the high impedance of the voltmeter. Only the voltage is measured between the two inner probes. Wire resistances, $R_{W2}$ and $R_{W3}$, and the contact resistances, $R_{C2}$ and $R_{C3}$, do not contribute to the measurement. Any measured voltage drop ($\Delta V$) will arise entirely from the sample resistance, $R_{S2}$. This simplifies matters as only $\Delta V$ and $I$ are needed to find the value of $R_{S2}$. 

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As stated the four-point probe works on the principle that the current passes through the sample and not through the voltmeter. This works if the impedance or resistance is considerably larger than the sample resistance. If one measures an insulating material, current may pass through the voltmeter and one measures the voltmeter impedance as opposed to the sample. In this work, we examine conducting/superconducting Nb, ideal for the 4-point probe set-up.
3 Exploring the impact of thickness on the superconducting properties of Nb and investigating the formation of a NbO(111) barrier layer

3.1 Thickness dependence on superconducting properties of Nb

3.1.1 Niobium as a Superconductor

The motivation for this portion of the study was in large part to fabricate thin films via MBE that demonstrated superconducting qualities. Once this was established the link between the film thickness and the superconducting critical temperature was further investigated in order to establish the minimum thickness of film that could be grown in the ATLAS and still return a superconducting transition.

First discovered in 1832\textsuperscript{86} niobium (Nb) is a lustrous, grey, ductile, paramagnetic transition metal. It is an effective micro-alloying element for steel, within which it forms niobium carbide (NbC) and niobium nitride (NbN). Despite the Nb content being small (typically, less than 0.1\%), the presence of these compounds improves the toughness, strength, formability and weldability of steel.\textsuperscript{87} These same niobium alloys are often used in pipeline construction.\textsuperscript{88}

Nb was chosen as the superconducting material used throughout this study due to its well documented superconducting properties, its high $T_c$, and its implementation in Josephson Junctions. At atmospheric pressure, it has the highest critical temperature of all elemental superconductors ($T_c = 9.2 K$). It has a London penetration depth of $\lambda_L = 39 \pm 5 \text{ nm}$ and a coherence length of $\xi = 38 \pm 5 \text{ nm}$.\textsuperscript{89} It is also one of three elemental Type II superconductors, alongside vanadium and technetium. These superconducting properties largely depend on the purity of the niobium.

Superconducting Nb compounds also see extensive use in the field. Niobium-germanium (Nb$_3$Ge), niobium-tin (Nb$_3$Sn) and other niobium-titanium alloys are used as type II superconducting wire for superconducting magnets.\textsuperscript{90} These magnets find use in magnetic resonance imagining instruments and particle accelerators.

3.1.2 Thickness and Superconductivity

Different superconductors exhibit different reactions to reduction of film thickness. For some, like Al or Sn, reducing the film thickness will increase $T_c$. For others like Pb, Bi or Nb, $T_c$ will decrease with thickness. L.N. Cooper predicted that in the limit of films thinner than the
coherence length with a very thin surface layer, $T_c$ can be expressed as

$$T_c(d) = T_c(\infty) \exp(-2a/d NV)$$  \hspace{1cm} (74)$$

where $T_c(d)$ is the transition temperature of a film of thickness $d$, $T_c(\infty)$ is the transition temperature in the bulk, $a$ is the thickness of the surface layer on each side of the film, and $NV$ is the bulk interaction potential ($NV_{Nb} = 0.32$). Studies by Wolf et al. have found measurements of the transition temperature of Nb grown on amorphous substrates such as fused quartz are in agreement with this equation. However, research by Kodama et al. found that the decrease in $T_c$ can vary when the substrates used are crystalline. These variations are plotted in Fig. 23.

Figure 23: log($T_c$) vs. $d^{-1}$ from rf sputtered Nb films upon six different substrates. The dotted lines show Wolf’s results. It can be seen that the lower the thickness of the film, the more unpredictable $T_c$ becomes. Adapted from Kodama et al. (1983).

As outlined by Strongin et al., there can be several influences on the value of $T_c$ but the most important was the interaction between metallic film and substrate. When depositing a metallic film on a substrate, the lattice of the metal is modified and adapts to the lattice of the substrate. This interaction modifies the superconducting properties. As film thickness increases, the film structure gradually restores its inherent crystalline structure. Research by Kodama found that for Nb films below a thickness of 30nm deposited on $\alpha$-Al$_2$O$_3$, the x-
ray diffraction patterns were affected by the surface structure of the substrate. Above 30nm, the patterns tended to converge to those inherent to Nb. The study concluded that the proportional decrease of $T_c$ with thickness was dependent on the crystallographic properties of the substrate surface and could be interpreted qualitatively by combined consideration of the growth, structure, and film resistance of the films at different thicknesses.

### 3.2 Fabrication and Analysis of Nb Thin Films

#### 3.2.1 Growth of Thin Films

Several substrates of Al$_2$O$_3$(0001) were prepared from a 4” Crystal-GmbH wafer. The wafer was cut into 1cm$^2$ substrates by a DISCO DAD3220 single axis dicing saw. Photoresist had been introduced to the surface of the wafer via spin-coating, a method where a few ml of resist are dispensed in the center of the wafer, which is typically brought to a rotational speed of several 1000 rpm. The centrifugal force will spread the resist into a uniform film across the surface of the wafer. The substrates were sonicated in acetone for 15 minutes to remove the layer of photoresist and then washed in isopropanol (IPA) for a further 15 minutes to remove any acetone residue. Upon being placed in the substrate holder mentioned in Section 2.1.1, the substrates were then placed under vacuum in the loadlock for up to an hour to ensure full evacuation had been achieved.

Upon transfer from the loadlock to the growth chamber, a current, $I_{fil}$, of 5.5A was passed through the tungsten filament to maintain a sample surface temperature of 490 ± 50°C. Temperature measurements were taken with an optical pyrometer leading to a wide margin of error. Six samples of thickness varying from 5nm to 50nm were grown on c-plane $\alpha$-Al$_2$O$_3$ under the following conditions:

<table>
<thead>
<tr>
<th></th>
<th>Sample A</th>
<th>Sample B</th>
<th>Sample C</th>
<th>Sample D</th>
<th>Sample E</th>
<th>Sample F</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Base Pressure (mbar)</strong></td>
<td>3.4×10$^{-10}$</td>
<td>3.2×10$^{-10}$</td>
<td>3.6×10$^{-10}$</td>
<td>8.1×10$^{-10}$</td>
<td>1.9×10$^{-9}$</td>
<td>6.8×10$^{-10}$</td>
</tr>
<tr>
<td><strong>Pressure after $I_{fil}$ (mbar)</strong></td>
<td>1×10$^{-9}$</td>
<td>1.5×10$^{-9}$</td>
<td>1.9×10$^{-9}$</td>
<td>2.4×10$^{-9}$</td>
<td>5.5×10$^{-9}$</td>
<td>1.2×10$^{-9}$</td>
</tr>
<tr>
<td><strong>Deposition Pressure (mbar)</strong></td>
<td>1.7×10$^{-8}$</td>
<td>1.2×10$^{-8}$</td>
<td>2.8×10$^{-8}$</td>
<td>4.4×10$^{-8}$</td>
<td>3.1×10$^{-8}$</td>
<td>2.2×10$^{-8}$</td>
</tr>
<tr>
<td><strong>Expected Thickness d (nm)</strong></td>
<td>5</td>
<td>10</td>
<td>20</td>
<td>30</td>
<td>40</td>
<td>50</td>
</tr>
</tbody>
</table>

Table 1: Parameters under which Nb thin films were grown. The associated error with pressure is $\Delta P = \pm 0.1 \times 10^{-8} \text{mbar}$, $\Delta I = \pm 1 \text{mA}$, and $\Delta d = \pm 1 \text{nm}$.
Base Pressure refers to the initial pressure of the vacuum system. Applying the current, \( I_{fil} \), to the sample holder has the unavoidable side effect of burning off any excess oxygen on the surface of the substrate causing a rise in pressure, recorded here as Pressure after \( I_{fil} \). The Deposition Pressure is the final pressure of the system once enough power has been supplied to the evaporator for deposition to begin. The deposition rate of Nb was maintained at 0.1Å/s for all growths. The expected thicknesses are taken from the thickness readings of the quartz crystal monitor.

Measurements of resistance against temperature were taken using the Sumitomo CCR mentioned in Section 2.2.6. The CCR has two sensors which take separate resistance readings at each time interval. The average of these is then taken to represent the resistance of the film. The associated error of these measurements was taken to be the standard deviation of the datasets, \( \sigma = 1 \times 10^{-5} \Omega \).

It should be noted that the value of the resistance of each sample prior to its superconducting transition varies due to the variations in contacts on the sample. The contacts are created at four separate points along the sample surface by hand. Silver paint is applied to adhere silver wire to these points. Due to there being no practical way to accurately replicate identical contacts for each sample, there will always be variations in contact size, distance between contacts, and contact positions along the sample leading to a difference in measured resistances.

### 3.2.2 Thickness Measurements

Before comparing the effect reducing the thickness had on the transition temperature, thickness measurements were taken using XRR. These can be seen in Fig. 24. The exception was Sample B which was erroneously used in the cryocooler before diffractometer measurements took place. When this section of the study was being conducted it was thought necessary to use a diamond scribe to scratch away oxide layers that may have formed on the sample surface before creating the contacts. This renders the surface unsuitable for XRR. It was later discovered that this was not necessary and contacts could be created on the sample surface without removal of any deposited material. In reality, the actual thickness of of Sample B may be lower than its expected thickness of 10nm.

<table>
<thead>
<tr>
<th></th>
<th>Sample A</th>
<th>Sample B</th>
<th>Sample C</th>
<th>Sample D</th>
<th>Sample E</th>
<th>Sample F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expected Thickness (nm)</td>
<td>5</td>
<td>10</td>
<td>20</td>
<td>30</td>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td>XRR Thickness (nm)</td>
<td>5.6</td>
<td>-</td>
<td>11.5</td>
<td>25.2</td>
<td>35.1</td>
<td>41.5</td>
</tr>
</tbody>
</table>

Table 2: Expected Thickness and thickness measured via XRR, \( \Delta d_{XRR} = \pm 0.1nm \)
Figure 24: The XRR scans of the thin films from the growth study. The potential formation of an Nb$_2$O$_5$ layer can be noted from these spectra by the effect a second layer has on oscillation periodicity and amplitude. The difficulty of fitting unknown parameters for this oxide layer can cause discrepancies in the fit.
The large variation between expected thickness and actual thickness comes from the geometry of the quartz crystal monitor (QCM). The QCM monitors the rate of deposition and amount of material deposited on its sensor, a quartz crystal microbalance, by measuring the change in frequency of the quartz crystal resonator. The sensor and sample cannot face the deposition source in the same direction as one would shadow the other so the rate of growth on one will not be equal to the rate of the other. The flux also differs between the two due to the inverse square relation. To compensate for this a ratio of these two rates, known as the tooling factor, is used to calibrate the QCM. The tooling factor can be adjusted by comparing the actual thickness value against the measured. For these growths, the tooling factor was incorrectly calibrated leading to a large variation in thickness.

The oscillations in the XRR spectra show shifts in periodicity and intensity which are indicative of a two layer film. It is possible that a second layer forms during growth or due to oxidation. Fitting of the XRR data aligns well with Nb$_2$O$_5$, an oxide that arises when Nb is oxidised in air.\cite{95} It is also one of the more common and robust Nb compounds. Further analysis via XPS to determine the composition of the films grown in ATLAS is described in Section 3.4.

### 3.2.3 $T_c$ of the thin films

Resistance-temperature curves obtained from measurements taken with the Sumitomo Cryocooler are shown in Fig. 26. The exact transition temperature, $T_c$, was obtained by taking the derivative of the resistance with respect to temperature around the region of interest, 4K – 10K. The rate of change will remain constant throughout the measurement until the transition temperature is reached, at which point the rate of change should spike. These spikes should correlate to $T_c$. Graphs of dR/dT can be seen in Appendix A.

<table>
<thead>
<tr>
<th></th>
<th>Sample A</th>
<th>Sample B</th>
<th>Sample C</th>
<th>Sample D</th>
<th>Sample E</th>
<th>Sample F</th>
</tr>
</thead>
<tbody>
<tr>
<td>XRR Thickness (nm)</td>
<td>5.6</td>
<td>-</td>
<td>11.5</td>
<td>25.2</td>
<td>35.1</td>
<td>41.5</td>
</tr>
<tr>
<td>Transition Temperature (K)</td>
<td>-</td>
<td>6.248</td>
<td>5.733</td>
<td>7.568</td>
<td>7.698</td>
<td>8.09</td>
</tr>
</tbody>
</table>

Table 3: Thickness and associated transition temperature. $\Delta T_c \pm 0.001K$, $\Delta d_{XRR} = \pm 0.1nm$

In line with findings from Kodama et al.\cite{93} we see a decreasing relation between thickness and $T_c$. A plot of log plot of $T_c$ against $1/d$ is shown in Fig. 25. Similar to Fig. 23, a linearly decreasing relation can be seen. For all films grown around the 30nm region, a more tightly bunched spread of data is seen, indicating the crystal structure of the film is more in line with the inherent crystal structure of Nb.
By extrapolation, for a sample of infinite thickness (i.e. $1/d = 0$), $\log_{10}(T_c) = 0.943$, therefore $T_c = 8.77 K$. This is in good agreement with the bulk ($T_c = 9.2 K$). Below 20nm, the low thickness dispersion from the expected relation is likely due to the structure of the film being heavily influenced by the substrate-film interaction.\(^{93}\)

Figure 25: $\log(T_c)$ vs. $d^{-1}$ for all Nb films grown on c-plane Al$_2$O$_3$

Although the correlation is as expected, there are still some points of interest to arise from this study. Studies by Il’in et al.\(^{96}\) show that for a sample of 9nm deposited by magnetron sputtering would correspond to a $T_c$ of 6.1K which aligns well with the $T_c$ recorded for sample B. However other measurements from Il’in’s study record higher a $T_c$ for much lower thickness when compared to our samples, such as one that records a $T_c$ of 8.2K for a 15nm film compared to 7.931K for our 34.5nm sample.
Figure 26: Resistance vs Temperature Measurements for the deposited films.
A possible explanation of this may arise from the presence of the aforementioned second layer in the films. Further evidence of the impurity of the films was garnered by calculating the Residual Resistivity Ratio (RRR). The RRR is the ratio of resistivity of a material at room temperature and at 0K. In the case of a superconductor, $\rho_{0K} = 0 \\Omega m$, so resistivity before the superconducting transition is taken instead. The RRR can vary strongly depending on the amount of impurities and overall quality of the sample.\textsuperscript{27} Resistivity is directly proportional to prevalence of defects, therefore a large RRR (300-400 has been reported for high purity Nb samples\textsuperscript{93}) is associated with a pure sample.

<table>
<thead>
<tr>
<th>Sample B</th>
<th>Sample C</th>
<th>Sample D</th>
<th>Sample E</th>
<th>Sample F</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>RRR</strong></td>
<td>2.8</td>
<td>1.9</td>
<td>2.6</td>
<td>4.0</td>
</tr>
<tr>
<td><strong>Associated Error</strong></td>
<td>0.2</td>
<td>0.1</td>
<td>0.3</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Table 4: Residual Resistivity Ratio. A full breakdown of the calculation of the RRR is detailed in Appendix B.

The low RRR returned for each film also points to the presence of a second layer. Previous studies by Ghazanfari \textit{et al.}\textsuperscript{99} have shown that the introduction of small amounts Nb$_2$O$_5$ into a bismuth strontium calcium copper oxide (BSCCO) superconductor will improve inter-grain connectivity which in turn will improve the superconducting critical current. However little change was observed in $T_c$. Therefore, there are likely other influences at play. It is also worth noting that at lower thicknesses, the potential oxide will make up a larger percentage of the film which may also have an effect on the observed transition temperature.

In Fig. 26f there is an initial drop to superconductivity at 9.02K followed by a gradual tapering off from 7.848K to 0 $\Omega$. Difficulties arise when trying to study the superconducting properties of bulk materials due to issues such as reduced coherence length, increased oxygen content or grain boundary contamination among others.\textsuperscript{100} Potentially, as we increase the size of the film, we introduce similar problems here that give rise to this smeared out transition.

No transition temperature was recorded for Sample A. It is possible that the transition temperature may occur below 4K and our system can't measure it. It is also possible that the sample is highly defective at this thickness given the high resistance seen in Fig. 26a indicating a possible lower growth limit for the ATLAS system between 5-11nm.

With the successful production of superconducting Nb, several unsuccessful attempts were made to develop a stepped surface to facilitate the fabrication of the novel JJ architecture. These are documented in Appendix C. Difficulties in producing the desired stepped surface, such as the need for a high level of control at sub 5nm feature sizes among others, led to refocusing efforts on developing a crystalline oxide barrier instead.
3.3 Oxidation of an epitaxial Nb thin film to form a NbO(111) barrier layer

3.3.1 NbO(111) formation in single crystal Nb

Niobium monoxide (NbO) is a metallic solid that can be formed by the oxidisation or high temperature annealing of Nb. Nb surfaces readily oxidise and the $T_c$ of Nb is found to drop by 1 $K$ per percent oxygen impurity.\textsuperscript{101} Dissolved oxygen will reside predominantly in interstitial octahedral sites.\textsuperscript{102} Sputtering can remove oxygen from the surface, however annealing will result in a diffusion of dissolved oxygen to the surface.\textsuperscript{103} The oxides that form on the Nb surface are heavily dependent on its orientation. When Nb(110) and polycrystalline Nb are oxidised, NbO initially forms on the surface,\textsuperscript{104–107} with niobium dioxide (NbO$_2$)\textsuperscript{104–106} and niobium pentoxide (Nb$_2$O$_5$)\textsuperscript{108–110} being observed at higher exposures. In the case of the Nb(001) termination, NbO$_2$ and Nb$_2$O$_{5-y}$ are observed\textsuperscript{111} but not NbO. In all cases, Nb$_2$O$_5$ is the furthest terminating oxide observed from metallic Nb.

Vacuum annealing reduces oxide surfaces. Nb$_2$O$_5$ can be reduced to NbO$_2$ at around 150$^\circ$C\textsuperscript{111} and subsequently NbO$_2$ can be reduced to NbO at around 300$^\circ$C.\textsuperscript{109,111} Oxidised Nb(110) and Nb(001) that are subsequently subjected to vacuum anneals are the only oxidised terminations that have been investigated by scanning tunneling microscopy (STM). Both show similarities with the formation of a regular array of one-dimensional NbO nanocrystals\textsuperscript{112,113} that are several nanometers in length.

Figure 27: Nishiyama-Wassermann Epitaxial Relation between Nb(110) and NbO(111) lattices. This image represents the unit cells and not all the atoms within it. Nb[001] aligns with one of the NbO $\langle 110 \rangle$ directions. The other two NbO $\langle 110 \rangle$ directions are rotated by 5$^\circ$ with respect to the two Nb $\langle 11 \rangle$ directions of the Nb(110) plane. Reproduced with permission from the author.\textsuperscript{115}
When oxidised Nb(110) is annealed, an NbO (111)-like layer forms on the surface.\textsuperscript{109,112–114} The NbO(111) plane is parallel to the Nb(110) and forms with either a Nishiyama-Wassermann or Kurdjumov-Sachs epitaxial relation with it.\textsuperscript{116} The NW epitaxial relation tends to dominate in the literature and is depicted in Fig. 27.

The APRG have analysed the structural and electrical properties of NbO,\textsuperscript{115} in particular investigating the annealing of a Nb single crystal. The Nb single crystal was annealed in an ultra-high vacuum environment at 850 °C for 1 hour. Large scale and atomic resolution STM images of the surface indicate the presence of two domains of nanocrystals of NbO terminated Nb(110). The presence of a monoxide is further evidence by XPS measurements where NbO is the only oxide observed. These measurements are in line with previous observations of this termination.\textsuperscript{112–114}

![Figure 28: (a) Illustrates terrace structure (b) Illustrates nanocrystal termination (c) Illustrates sole presence of monoxide. Adapted from Zhussupbekov (2020)](image)

Although NbO(111) has been successfully produced on single crystal Nb, the motivation for this section is to produce it on a (110) oriented Nb thin film. To probe the validity of using NbO(111) as a barrier layer, it is valuable to demonstrate it is a good candidate for a tri-layer without needing to perform JJ characterisation. The most important aspects to explore are barrier crystallinity, epitaxial relationship to Nb(110), homogeneity of the layer, and its electronic properties.
3.4 XPS Analysis of Nb(110) thin film

3.4.1 Prior to the anneal

The film selected for this section of the project is Nb-22. It was grown in UHV on c-plane Al₂O₃ at a substrate temperature of 600°C and a pressure of 7×10⁻⁷ mbar. An XRD of the surface indicates a (110) orientation. There is evidence of the (111) orientation with the presence of the (222) reflex but (110) dominates. The surface was oxidised by exposure to the atmosphere.

![XRD spectrum of Nb-22 thin film](image)

Figure 29: XRD spectrum of Nb-22 thin film. The film is 110 oriented.
A survey scan of the surface was taken. The initial scan indicates the presence of O, C and Nb as expected. A thin layer of carbonaceous material is usually found on the surface of most air exposed samples, known as adventitious carbon. Adventitious C generally appears at 284.8 eV (variations exist 285.0 eV and 284.5 eV). This provides a convenient reference point if the spectrum is shifted for any reason and the C 1s peak is usually set as the reference peak for analysis. Adventitious C is generally comprised of a variety of carbon species with small amounts of both singly and doubly bound oxygen functionality. Indeed, measurements prior to the anneal indicate a mix of C-C, C-O and C=O bonds present in the adventitious C composition.

As stated the O 1s peak is also present. Interpretation of O 1s spectra is not straightforward. These peaks tend to be broad with multiple overlapping components. The O 1s binding energy of many compounds and species falls within a very narrow range. The spectrum presented in this report likely suggests the presence of Nb$_2$O$_3$ in the composition of the O$_{1s}$ but it is difficult to say with absolute certainty. Spectra for C and O prior to the anneal are included in Appendix D.
The core-level binding energies of Nb and its oxides reported in literature are summarized in Table 5.

As can be seen in Fig. 31, the composition of Nb is a mixture of various oxides and pure metallic niobium. Due to spin-orbit interaction, most of the components are split into doublets, a composite quantum state of a system with an effective spin of $\frac{1}{2}$, such that there are two allowed values of the spin component, $-\frac{1}{2}$ and $+\frac{1}{2}$. The doublet Nb 3d$^{3/2-5/2}$ has a higher energy level for the angular momentum state $j = \frac{5}{2}$ and a lower one for $j = \frac{3}{2}$. The metallic Nb is fit with an asymmetric convolution of the Gaussian-Lorentzian (GL) lineshape. The
oxides are fitted with the standard GL lineshape.

The most prevalent component is the pentoxide as expected. Nb(110) thin films that are oxidised in atmosphere at room temperature tend to form a 20-50Å amorphous Nb$_2$O$_5$ layer\textsuperscript{124}. Also present are the suboxides, NbO$_2$ and NbO, in addition to metallic Nb itself. The presence of these oxides in this film is a good indication that they were present on the films grown in the previous half of this chapter. In addition, NbO$_2$ and Nb$_2$O$_5$ are very rough surfaces\textsuperscript{125} which may help explain the shape of the XRR scans in Fig.\textsuperscript{24}.

### 3.4.2 First Anneal: 700$^\circ$C for 2 hours

Nb-22 was annealed for 2 hours at a temperature of 700$^\circ$C at a pressure around $10^{-8}$ mbar. A survey scan is shown below.

![Survey Scan of Nb-22 Surface post 1$^{st}$ anneal.](image)

As expected, there is a sharp increase in the Nb composition of the film with reductions in O and C content.
Fig. 33 depicts the XPS measurements of the Nb 3d peak immediately following the first anneal. As expected, the anneal has successfully reduced Nb$_2$O$_5$ and NbO$_2$ to NbO, however when an attempt was made to fit the data to solely Nb and NbO, the fit was found to be insufficient. Two lineshapes were added to accommodate this additional component. It was determined that the additional components were niobium carbide (NbC) that had formed during the anneal. The exact stoichiometry of the carbide is unknown but the $5/2$ and $3/2$ components have been previously reported around 203 eV and 206 eV$^{120,126}$ The C 1s peak in Appendix E also indicates the presence of two carbon states, likely adventitious C and NbC.

As mentioned, XPS fitting uses the adventitious C peak as a reference point due to its prevalence and well documented 284.8 eV binding energy. Initially, adventitious C was attributed to the wrong peak in the C 1s spectrum. This lead to an offset in the Nb spectrum and the peaks which we now know correspond to Nb and NbO were initially thought to correspond to NbO and NbO$_2$ respectively. It was then thought that the additional lineshapes might represent an intermediate bonding state, an interfacial state for the Nb atoms located at the NbO/Nb interface. Previous work by Ma et al. reported the presence of Nb$_2$O$_3$ underneath NbO$_2$ for a Nb(100) single crystal oxidized by air and annealed at ~ 150°C$^{111}$ The incorrect assumption that the composition of Nb was solely oxides prompted a second anneal.
3.4.3 Second Anneal: 680°C for 14 hours

Following the first anneal, the sample was left under vacuum in the chamber for 14 days. Standard procedure is to take a survey scan and more in-depth scans of Nb 3d, O 1s and C 1s to ensure the surface has not changed. These scans are included in Appendix [F]. When analysis of these spectra was undertaken, a shift of binding energies from the assumed NbO$_2$ and NbO peaks to the NbO and Nb peaks was observed. Given that the phases changing so greatly under vacuum was virtually impossible, a reassessment of the spectra from the first anneal was undertaken. At this juncture, the fits were updated to reflect the presence of NbC. No change to the composition of Nb was noted. There was an increase in the amount of adventitious C present on the sample which was unexpected. As other users have access to the system, it is possible that adventitious C was introduced to the system via the transferral of new samples into the chamber, particularly if any of those samples use carbon tape.

A second anneal at 680°C was performed for 14 hours though it yielded virtually identical results to the first anneal annael.

![Figure 34: XPS Spectrum of Nb 3d Peak post 2nd anneal.](image)

There is a slight decrease in oxide content compared to the previous anneal ($\sim 37\%$ compared to $\sim 43\%$), however it could be attributed to errors in the fit. Likewise, there is an increase in the carbide content of the film (from $\sim 10\%$ to $\sim 16\%$). The anneal seems to have strengthened the presence of NbC throughout the entire film. Measurements of the C 1s peak indicate the possibility that all adventitious C has been removed leaving NbC. This can be
3.4.4 Sputter and Third Anneal: $680^\circ C$ for 16 hours

In an attempt to remove the carbide in the sample, the film was subjected to a sputtering. Sputtering is performed under vacuum in the XPS chamber, where ions of Ar are accelerated towards the surface of the substrate. These high energy ions bombard the surface removing material to some desired depth. It is also known as ion milling. Sputtering is known to preferentially remove oxides so the film was subjected to a third anneal post sputtering. Prior to the sputter, the sample was left under vacuum for two weeks. Again, scans of the surface were taken and can be found in Appendix H. The sample was sputtered for 15 minutes with $750eV$ ions accelerated with a current of $8\mu A$ at a pressure of $1.1 \times 10^{-5} mbar$.

![Survey Scan 6 Post Sputter (15min, 730eV, 8\mu A)](image)

Figure 35: Survey Scan of Nb-22 post sputter
As expected, the sputtering has removed any oxides that were present in the film. It has increased the carbide content of the film substantially as NbC now accounts for more of the Nb composition than metallic Nb (∼44% to ∼56%). It is not surprising that the carbide resisted sputtering. Previous studies have indicated that relative to borides, nitrides or oxides, the core level spectra of transition metal carbides are relatively unaffected by Ar sputtering with no preferential sputtering of C observed\cite{128}. The subsequent anneal resulted in the return of NbO likely as a result of dissolved oxygen in the lattice being brought to the surface. These results are documented in Appendix I. \[1\]

Although reducing the oxides formed on the surface of an Nb film exposed to atmosphere is a somewhat trivial affair, the formation of a carbide on the surface and has proven to be a significant obstacle in realising an NbO(111)-terminated Nb(110) thin film. It could be possible to utilize the carbide as a barrier layer however further study of this would be required. The LEED analysis in Section 3.5 indicates that the carbide may be ordered.
3.5 LEED Analysis of Nb(110) thin film following high temperature anneal

Figure 37: LEED Images post anneal 1 (a) 69eV (b) 99eV (c) 135eV

Figure 38: LEED Images post anneal 2 (a) 69eV (b) 99eV (c) 135eV

Figure 39: LEED Images post anneal 3 (a) 69eV (b) 99eV (c) 135eV
LEED images were taken following each anneal. The parameters used for each set of images are documented in Appendix J. In the study by Zhussupbekov et al. examining vacuum annealed Nb(110) which was oxidised prior to the anneal, the LEED images have been characterised by a superposition of the Nb(110) and NbO(111) diffraction patterns that are indicative of the NW epitaxial relation. Nb(110) is pseudo-hexagonal and when overlayed on hexagonal NbO(111), the misfit gives rise to spot splitting. This LEED image can be seen as an inset in Fig. 28(c).

From a qualitative analysis of the images in Figs 37, 38 and 39, we see an increase in crystallinity from the first anneal to the second but the results from the second to the third anneal are similar. It may be that the crystallinity did not improve significantly between these anneals or that the sputtering the film was subjected to prior to the third anneal reduced the crystallinity which was restored by the third anneal. We do not see the spot splitting observed by Zhussupbekov. However, we can see the presence of two hexagonal patterns, most noticeable after the second round of annealing.

Figure 40: LEED Image (Beam energy = 69eV) captured after second anneal indicating two hexagonal patterns.

The patterns are rotated from each other through an angle of 30°. The brightness of the larger hexagon could result from the coincidence of the two patterns or it could be a separate structure. However, it could be a combination of both explanations. The larger hexagon is always of a higher intensity, indicating that yellow and orange are separate crystal structures.

Increasing the beam energy of the LEED increases the electron mean free path. At 135eV, the yellow unit cell dominates. This can be interpreted at the yellow structure being further from the surface termination, indicating that it may be Nb(110).
4 Preparation of NbN for use in a spin-triplet superconductor

4.1 Spin Triplet Superconductivity

4.1.1 Ferromagnetic Superconductors and the Coexistence Problem

A ferromagnetic superconductor is a material that displays an intrinsic coexistence of ferromagnetism and superconductivity. Both concepts were initially thought to be mutually repulsive until Ginzburg \[^{[3]^29}\] postulated that there was a possibility of coexistence under the condition that the magnetization was less than the thermodynamic critical field.\[^{[2]^29}\]

Ginzburg viewed the problem in terms of the "orbital mechanism", in which the interaction between charged Cooper pairs and the vector potential of the internal magnetic field suppresses the superconductivity. In 1958, Matthias et al.\[^{130}\] proposed that there was an additional mechanism at play, the quantum mechanical exchange interaction, the phenomenon whereby an individual atomic magnetic moment will attempt to align all other atomic magnetic moments within a material with itself. The interaction tries to align electron spins in a ferromagnet whereas the spins of the two electrons in the Cooper pair are antiparallel. These antagonistic spins lead to the effect of paramagnetic pair breaking.

When the paramagnetic effect is sufficiently large enough, there are two options for the Cooper pair. It can become an equal-spin pair, where the two spins point in the same direction as the magnetization vector or it can keep its spins pointing in opposite directions with respect to the magnetization vector causing it to acquire a non-zero center-of-mass momentum. This second possibility was independently discovered by Fulde and Ferrell at the University of Maryland\[^{131}\] and Larkin and Ovchinnikov at the Moscow Physico-Technical Institute.\[^{132}\] It is known as the FFLO state.

The spin-spin interactions in a ferromagnet cause the electronic bands for up spins and down spins to shift with respect to each other by an amount of $2E_{ex}$. The exchange splitting shifts the momenta at the Fermi energy, $E_F$, from $k_F$ to two new positions; $k_{F1} + Q/2$ and $k_{F1} - Q/2$ where $Q$ is the center-of-mass momentum. Two electrons at $E_F$ with opposite spin will form a Cooper pair with $\pm Q$.

In the absence of exchange splitting, Cooper pairs in most common superconductors prefer the singlet state ($\uparrow \downarrow - \downarrow \uparrow$). When exchange splitting is introduced, the two spin contributions to the amplitude of the Cooper pair are proportional to $e^{\pm i(k_{F1} - k_{F1})\cdot R}$. The resulting state is a mixture of singlet and triplet spin states with zero spin projection on magnetization axis, i.e.

\[^{3}\]Of Ginzburg-Landau theory fame, Section 1.1.6
opposite spins\textsuperscript{133}

\[(\uparrow \downarrow - \downarrow \uparrow) \rightarrow (\uparrow \downarrow e^{iQ \cdot R} - \downarrow \uparrow e^{-iQ \cdot R}) = (\uparrow \downarrow - \downarrow \uparrow) \cos(Q \cdot R) + i(\uparrow \downarrow + \downarrow \uparrow) \sin(Q \cdot R) \quad (75)\]

In summary, when the spin-singlet Cooper pairs of a standard superconductor enter a ferromagnetic material, the spin-splitting of the energy bands of the ferromagnet give rise to opposite-spin triplets as spin-up and spin-down electrons acquire different phases upon propagation.

4.1.2 The Proximity Effect and Proximity Structures

The FFLO state rarely exists in nature. Out of thousands of superconducting candidates, only a handful, such as the heavy-fermion material CeCoIn\textsubscript{5}\textsuperscript{134} are known to exhibit the FFLO state. However, the existence of FFLO-type states has been established in ferromagnetic metals in contact with superconductors\textsuperscript{135} These heterostructures are known as FS proximity structures and they exist as a result of the proximity effect.

The proximity effect is the "leaking" of superconductivity when a superconductor is in contact with a normal non-superconductor. In essence, the Cooper pairs of the superconductor will diffuse into the non-superconductor over a distance that depends on the disorder in the non-superconductor and the temperature. It was first discovered by Holm and Meissner\textsuperscript{136} in 1932 and the theory was developed by de Gennes\textsuperscript{137} The flow of a supercurrent in an SNS or SIS JJ is possible due to the proximity effect.

The generation of singlet to triplet spins in an FS proximity structure can be manipulated by adjusting the misalignment between the two ferromagnets\textsuperscript{135} Controlling the singlet to triplet conversion will allow for control of the superconducting condensation energy and $T_c$\textsuperscript{138,140}. However, in an F/S/F structure, the field inside a superconductor is suppressed\textsuperscript{141} resulting from the ferromagnetic exchange fields favouring antiparallel alignment of the ferromagnets. Restructuring these layers into a S/F/F configuration causes this effect to become less prominent\textsuperscript{142,143} but requires the orientations of the ferromagnets be tuned independently. It is preferable to reduce the number of magnetic elements required to tune $T_c$ in order to minimize any stray fields arising from the proximity structure.

An antiferromagnet can provide a magnetic structure with no net magnetization\textsuperscript{145}. Anti-ferromagnets will not emit an external field, therefore avoiding vortex formation and demagnetizing currents when coupled to a superconductor. The magnetization of the adjacent ferromagnet can be easily controlled. Applying a magnetic field will not affect the magnetic
moment of an antiferromagnet. Studies of the Josephson effect, $T_c$ and the critical field in uncompensated (i.e. antiferromagnetic magnets where magnetic moments along the surface are not compensated) superconductor-antiferromagnet structures have proved antiferromagnets to be applicable for manipulating the superconducting state, despite their zero net magnetization. Although most studies focus on uncompensated antiferromagnetic interfaces, Johnsen et al. have also demonstrated theoretically that proximity coupling of a compensated antiferromagnetic interface to an FS structure in an AF/S/F formation can allow for the modulation of $T_c$ and the control of the superconducting phase.

To the best of the author’s knowledge most studies of AF/S/F trilayer structures are theoretical and largely material independent. In structures where the Cooper pair tunnels through a non-superconducting barrier, the spin triplet spatial decay constant is smaller in comparison to the standard zero spin, zero centre-of-mass momentum Cooper pair. This combined with the spin polarized nature of the spin triplet state, make it interesting to modern electronics. Investigating the mechanics of such a trilayer with a superconducting layer, such as niobium nitride (NbN), could potentially lead to some novel results.

### 4.1.3 Niobium Nitride (NbN)

Niobium nitride is a transition metal nitride. These are a class of materials materials known for their mechanical properties. They have a metallic thermal and electrical conductivity, on the order of magnitude of pure metals, and many of them are superconductors. NbN is a crystalline material that crystallizes in an NaCl type configuration. The superconducting properties of NbN were first documented by Ashermann et al. The NbN system is complex and has various phases such as $\beta$, $\delta$, $\epsilon$, $\gamma$, $\delta'$ and $\eta$. The most commonly studied phase is the cubic $\delta$ phase. It has the highest $T_c$ of the binary compounds with an NaCl structure ($T_c = 17.8K$). It also has a high London penetration depth and coherence length ($\lambda_L = 420nm$, $\xi = 6.5nm$).
4.2 NbN Growth by magnetron sputtering

4.2.1 Preparation of NbN Thin Films

Growth of NbN thin films in the ATLAS system is not as simple as evaporating a puck of NbN as niobium and nitrogen evaporate incongruously resulting in a different stoichiometry of the film. A source of nitrogen to replace that which is lost would be required but leaking nitrogen gas ($N_2$) into the chamber would also not suffice as it is very non-reactive. A plasma source used in conjunction with $N_2$ would be able to split the gas into reactive N atoms but adapting the ATLAS for this would require the purchase and installation of several nitrogen compatible components. DC magnetron sputtering is a more suitable method as the plasma involved splits $N_2$ and growth of NbN thin films by this process is widely documented.

Five $1\text{cm}^2$ substrates of c-plane Al$_2$O$_3$ were prepared in the standard way; sonicated for 15 minutes in acetone followed by a further 15 minutes in IPA. A Nb (99% purity) metallic target, $2'' \times \frac{1}{4}''$ thick, was mounted at the top of the chamber which was evacuated to a base pressure around $2 \times 10^{-5}\text{mbar}$. The substrates were placed in the loadlock which was pumped to a comparable pressure to the chamber before transferral into the chamber. Once loaded, the substrate heater was adjusted incrementally to an appropriate temperature (dependent on growth recipe). The system was then left for an hour to allow the pressure and temperature to stabilise.

Once stabilised, Ar gas was introduced to the system at a gas flow rate of 60 sccm. The flow rate is high in order to ignite the plasma source. Once ignited, the gas flow rate was lowered to 30 sccm. The deposition power was then set before introducing $N_2$ gas into the system (again, dependent on the growth recipe). The target was presputtered for 10 minutes to ensure a flow of Nb before the shutter concealing it was opened. A film was then grown over a 30 minute window. The first 5 films were grown closely adhering to a growth recipe for superconducting $\delta$-NbN with a [111] preferred orientation utilised by Xin-kang et al.

<table>
<thead>
<tr>
<th></th>
<th>NbN-1</th>
<th>NbN-2</th>
<th>NbN-3</th>
<th>NbN-4</th>
<th>NbN-5</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pressure after Ar (mbar)</strong></td>
<td>1.70×10^{-4}</td>
<td>1.50×10^{-4}</td>
<td>5.04×10^{-4}</td>
<td>5.70×10^{-4}</td>
<td>4.54×10^{-4}</td>
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<td><strong>Deposition Pressure (mbar)</strong></td>
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<td>1.47×10^{-3}</td>
<td>2.0×10^{-3}</td>
<td>8.7×10^{-4}</td>
<td>2.3×10^{-3}</td>
</tr>
<tr>
<td>$N_2$ (sccm)</td>
<td>4.5</td>
<td>6.0</td>
<td>8.0</td>
<td>2.0</td>
<td>4.5</td>
</tr>
<tr>
<td><strong>Temperature (°C)</strong></td>
<td>739</td>
<td>732</td>
<td>728</td>
<td>734</td>
<td>759</td>
</tr>
</tbody>
</table>

Table 6: Parameters under which NbN thin films were grown. Deposition power was kept constant at 60W. The associated error with pressure is $\Delta P = \pm 0.01 \times 10^{-3}\text{mbar}$, $\Delta T = \pm 1\degree C$, $\Delta N_2 = \pm 0.1\text{sccm}$, and $\Delta$ Power = $\pm 1W$
The first three growths increase the ratio of N$_2$ to Ar while the fourth growth reduces the amount of N$_2$ present during growth. The fifth growth returns to the flow rate of the first growth but increases the temperature by 20$^\circ$C to investigate the effect, if any, it has on the film.

### 4.2.2 Temperature Measurements of NbN Films

Resistance versus temperature measurements were taken with the cryostat. Due to damage sustained to Temperature Sensor A, Sensor B had to be used. It is located below the sample and in practice will record a slightly higher temperature than that of the sample however the difference should be negligible and it should still record a transition in the superconducting regime of NbN.

Resistance versus temperature measurements of the first five samples can be seen in Fig. 43. No superconducting transition was detected. Initially, the resistance of NbN trends upwards as the temperature is decreased. This has been observed in other work documenting its transition. Transition metal nitride superconductors and especially NbN are generally not considered as good metals despite having some of the largest superconducting energy gaps and $T_c$ among conventional BCS superconductors. Thus it is not unusual for NbN to behave as an insulator (i.e. $R$ increasing as $T \to 0$) before reaching its superconducting transition. We do see a rapid increase in resistance, particularly for Fig. 43a and 43b as temperatures fall below 50K. How much this relates to the quality of the film or with the contacting of the film is unclear. A less substantial increase is noted in the remaining substrates but, as stated, no transition has occurred.

The superconducting properties of NbN are strongly dependent on the formation of the correct crystallographic phase. There are four NbN phases that are superconducting, $\delta$ as mentioned, hexagonal $\epsilon$ ($T_c = 11.6K$)[172] tetragonal $\gamma$ ($T_c = 12 - 15K$)[173] and hexagonal $\beta$-Nb$_2$N ($T_c = 0.35 - 0.6K$)[174] All other phases are non-superconducting including the $\delta'$ phase and other higher order nitrides like Nb$_4$N$_5$ and Nb$_5$N$_6$[175] The various phases of NbN$_x$ all exist in different stoichiometries.[176]

(a) $\beta$-Nb$_2$N, $x = 0.4 - 0.5$

(b) $\gamma$-Nb$_4$N$_3$, $x = 0.75 - 0.8$

(c) $\delta$-NbN, $x = 0.88 - 0.98$ and $1.015 - 1.062$

(d) $\epsilon$-NbN, $x = 0.92 - 0.1$

(e) $\delta'$-NbN, $x = 0.96$
Fig. 42 relates the phases of NbN to their stoichiometries.

Determining the correct phase of NbN present in the samples will be crucial in identifying the steps required to amend the deposition process.
Figure 43: Resistance vs Temperature Measurements for the deposited films. Sensor B is used to record temperature.
4.2.3 XRD Analysis of Thin Films

In the $\delta$ phase, we would typically expect to see the two characteristic peaks of NbN, the (111) and (200) reflections. Their position (degree) is dependent on the substrate $^{177}$ Other peaks corresponding to the (220), (311), (222), (400) and (331) reflections respectively have also been observed albeit not all on c-plane Al$_2$O$_3$ substrates $^{178,179}$ The XRD spectrum from 20° to 120° was recorded for each sample.

![XRD Spectrum of NbN-1](image)

**Figure 44:** XRD Spectrum of NbN-1. In the interest of clarity, the peaks from the sample stage have gone unlabelled but they occur at 44.34°, 64.58°, 77.55° and 98.35°.

In the spectrum of NbN-1, we see what could be the first characteristic peak NbN(111) of $\delta$-NbN and the NbN(222) reflex. NbN(220) is also present, although very weakly. NbN(111) is offset greatly from it’s expected value of 35.2° $^{179}$ for $\delta$-NbN grown on c-plane Al$_2$O$_3$. This offset may be the result of in-plane tensile strain. The lattice mismatch between NbN and c-plane Al$_2$O$_3$ is relatively high ($a_{\text{Al}_2\text{O}_3} = 4.77\text{Å}$, $a_{\delta-\text{NbN}} = 4.39\text{Å}$),

$$\text{mismatch} = \frac{a_{\text{sub}} - a_{\text{film}}}{a_{\text{sub}}} \times 100 \approx 8\%$$
However, it is far more likely that this peak corresponds to $\gamma$-Nb$_4$N$_3$. A study by Wright et al.\textsuperscript{174} indicates the Nb$_4$N$_3$ (112) reflex occurs around 35.6°. $\gamma$-Nb$_4$N$_3$ is a stable tetragonal phase that is related to the $\delta$ phase by removal of half the nitrogen atoms in alternating planes along the c-axis. Utilizing the information in Fig. 42, the ratio of Nb:N is $\approx$ 1:0.75.

There are other regions of interest in the spectrum. Around 65.5°, there is a peak that doesn’t align with any $\gamma$ or $\delta$-NbN reflections. Previous works on NbN growth have indicated that it is possible for a mixture of phases to exist in one film.\textsuperscript{180} This peak may correspond to $\beta$-Nb$_2$N (103).\textsuperscript{181} Although $\gamma$-Nb$_4$N$_3$ is superconducting in a regime that the cryostat can measure, the introduction of other phases in the film is likely influencing its superconducting properties.
Figure 47: XRD Spectrum of NbN-2. A reduction in peak intensity potentially indicates a reduction in crystallinity.

Figure 48: XRD Spectrum of NbN-3. The characteristic (200) reflection is potentially present, albeit weakly.

Notably in the NbN-2 and NbN-3 spectra we see much better alignment of the NbN(111) and NbN(222). The intensity of the NbN(222) peak is reduced from NbN-1 but given that we
are comparing potentially different phases of NbN, a direct comparison may be inappropriate at this stage. In NbN-3, the possible (but very weak) presence of the second characteristic peak, NbN(200) can be observed. An enhanced view of the NbN(111) peaks from NbN-2 and NbN-3 are provided in Fig. 49.

![Enhanced view of NbN(111) from NbN-2 and NbN-3.](image)

Figure 49: Enhanced view of NbN(111) from NbN-2 and NbN-3.

In the aforementioned Xin-kang et al.\(^{168}\) study, nitrogen flow rate was increased to optimize the produced films. In that study, a ratio of 20 parts Ar to every 3 parts N\(_2\) (50:7.5) was deemed optimal although there is no reference to films grown at higher N\(_2\) ratios. In a study by Wen et al.\(^{182}\) higher N\(_2\) flow rates (> 15 sccm) would lead to a formation of mixed δ and δ' phase films. The reason behind the observation of more definite δ-NbN peaks is obvious; as expected a higher concentration of N\(_2\) has shifted the phase from γ-Nb\(_4\)N\(_3\) to a phase more in line with δ-NbN. The anomalous peak around 65° is still present in the scans indicating the likely presence of β-Nb\(_2\)N.
Figure 50: XRD Spectrum of NbN-4.

Figure 51: XRD Spectrum of NbN-5.
NbN-4 and NbN-5 returns a similar spectrum to that of NbN-1, likely due to their near identical growth parameters. From observation alone, increasing the temperature does not seem to have significantly altered the growth substantially. It is likely that a temperature increase of 20°C is too small to generate any significant changes during the growth process. Upon closer inspection, the alignment of the Nb₄N₃(112) peak is more in line with the results of Wright et al. The extent that this is affected by the temperature of the substrate is unclear as the Nb₄N₃(112) peak of NbN-4 is also better aligned but was grown at a comparable temperature to NbN-1. The study from Wright indicates that films grown at 650°C produced γ-Nb₄N₃ films with a (112) orientation. Increasing the temperature to 800°C in increments of 50°C gradually shifted the phase from γ-Nb₄N₃(112) to δ-NbN(111) and finally to ε-NbN(100). Increasing the temperature beyond this point would again shift the phase from ε-NbN(100) to δ-NbN(111), then to γ-Nb₄N₃(112), and finally β-Nb₂N(002).

A graphic summation of all XRDs presented in this section is depicted in Fig. 53. An enhanced view of all XRD peaks in the vicinity of 35° is taken from this image and is seen in Fig. 52.

![Enhanced view of NbN(111)/Nb₄N₃(112) Peaks](image)

Figure 52: Enhanced view of NbN(111)/Nb₄N₃(112) Peaks. Y-axis is augmented to include all spectra.

The overlay of spectra indicates an obvious conclusion; increasing the N₂ content during growth will shift the phase from γ-Nb₄N₃ to δ-NbN. This is most apparent in the alignment of NbN-3 (the most nitrogenated film) to the NbN(111) peak. In addition to increasing the nitrogen content, there are other considerations to be taken in revising the growth process such as crystallinity, substrate temperature and the presence of β-Nb₂N which, from observation
alone, does not seem to be affected by any of the changes made during the course of this study. However, if $\beta$-Nb$_2$N is present in the film, it may be possible to convert its phase by post-annealing.

Figure 53: All XRD Spectra for NbN Samples. Y-axis is augmented to include all spectra.
4.2.4 Post annealing of NbN-1

Post-annealing is an important technique in thin film fabrication, which can help enhance the properties of the thin film by changing the microstructure and stoichiometry. In a study by Shy et al.\textsuperscript{173} NbN films grown at substrate temperatures above 600°C were epitaxial, those between 600-300°C were polycrystalline, and below 300°C were amorphous. Polycrystalline and amorphous films were subjected to an 800°C anneal for 30 minutes. This resulted in a crystallisation of the films, an increase in $T_c$ for previously superconducting films and the onset of superconductivity for previously non-superconducting films. These results can be seen in Fig. 54.

![Figure 54: Annealing can transform a nonsuperconducting film into a superconducting one. Adapted from Shy (1973)\textsuperscript{173}](image)

A study by Hotový et al.\textsuperscript{183} monitored the effect of rapid thermal annealing (RTA) on NbN films on GaAs substrates. In their research, they compared the anneals of amorphous NbN (2%, 5% and 20% nitrogen content) and polycrystalline (10% and 15%). Following an RTA of 850°C for 10s, the 2% amorphous sample stayed amorphous but the 5% sample changed to $\delta$-phase NbN. The 10% sample remained as is but its lattice parameter decreased, likely due to the removal of nitrogen content from the lattice. The 15% and 20% films converted from NbN to tetragonal-Nb$_4$N$_3$. It is possible that during annealing, interstitial nitrogen is removed from the lattice which is then distorted into the tetragonal phase.

Annealing of NbN-1 took place in a vacuum chamber. The film was annealed at 800°C for a 30 minute period at a pressure of $7\times10^{-6}$ mbar. The temperature-resistance curve is shown in Fig. 55.
As can be seen in Fig. 55, the anneal was unsuccessful in transforming NbN-1 into a superconducting film. However there is a significant reduction in resistance. This may indicate an improvement in film quality but it could also be a result of the contacting of the films \[xii\].

Regrettably, the diffraction pattern of this film could not be recorded due to an alignment issue with the Bruker D8 Diffractometer. The apparatus was not in working condition by the conclusion of this project. Without being able to quantify the change brought about by annealing the films, this avenue of the project was abandoned in favour of revising the growth process.

\[xii\] See Section 3.2.1
5 Discussion and Future Work

With every mistake,  
We must surely be learning.  

\[ \text{The Beatles} \]

\[ \text{While My Guitar Gently Weeps} \]

5.1 NbO(111) Termination

A NbO terminated Nb(110) thin film was not realised during this project. The unexpected formation of NbC on the surface has provided a significant stumbling block and it is crucial that efforts are focused on methods to remove it if the project is to proceed any further. Sputtering of the surface did not aid in this and only served to remove any oxides present. A high temperature anneal may be an appropriate avenue to investigate. A study from Cooper et al. found that when metals such as molybdenum or tungsten were machined by electrical spark discharge, surface layers containing carbide phases of various compositions would form. They were able to remove these carbide layers by annealing the metals at 2000°C for 1 hour in reducing environments such as Ar. Attempting anneals at such temperatures would require utilising the group’s Scanning Tunnelling Microscope (STM), a device that can achieve higher temperatures than the Omicron XPS.

If a successful NbO(111) termination can be produced on a Nb(110) thin film, that will be a novel result. However, there will be more work required in assuring the it is a good candidate for a tri-layer without the need for JJ characterisation. The barrier crystallinity and epitaxial relationship to Nb(110) can be probed in via XPS and LEED. In order to get a rough idea of the unit cells giving rise to the patterns seen in the LEED, the LEED will need to be calibrated by measuring a clean, ordered Nb single crystal at the same energies and LEED geometry.

As mentioned utilizing NbC as the barrier layer may also be a possibility but further study of NbC and its suitability in a superconducting heterostructure is required.

5.2 NbN Superconducting Film

Comparison between the five samples of NbN strongly indicate that the recipe used is lacking in one or more aspects. In order to produce a superconducting NbN film, in particular a δ-NbN film, revisions to the growth process will be necessary. One possible revision worth investigating is modulation of the Ar flow rate. The Ar flow rate was kept constant throughout each growth (30 sccm). Minimization of the Ar pressure relative to the N\textsubscript{2} pressure has been known to produce better quality films with less stress.

Another revision that could be investigated in the future growth of NbN films is the selection
of substrate. Depositing NbN films to substrates with a considerable discrepancy in unit cell parameters relative to NbN results in the deterioration of superconducting properties. The use of Si as a substrate for NbN films has been adopted and features advantageous properties from a processing point of view but as a result of its significant lattice mismatch with NbN ($a_{Si} = 5.43\,\text{Å}$), only polycrystalline films not exceeding $T_c \approx 10\,\text{K}$ at 5$\text{nm}$ have been produced.\textsuperscript{187,189}

Although c-plane sapphire has a low lattice mismatch to NbN, there are better matched substrates. (100) oriented MgO is a commonly used substrates for constructing NbN thin films. It has a similar lattice parameter ($a_{MgO} = 4.21\,\text{Å}$). It is also crystalline lattice matched for epitaxy of very thin NbN films in the superconducting regime.\textsuperscript{190} Downsides to the use of MgO are its relatively expensive cost and its hygroscopic properties that can lead to the deterioration of films.\textsuperscript{167} Titanium nitride ($a_{TiN} = 4.23\,\text{Å}$) and r-plane $\text{Al}_2\text{O}_3$ also see use as substrates.

Post annealing is still another option at this point. It was initially considered to anneal the films in a $\text{N}_2$ atmosphere, however previous studies indicate that thermal annealing of sputtered NbN thin films in $\text{N}_2$ degrades their superconducting properties.\textsuperscript{190} 100% pure $\text{N}_2$ will also not exclude $\text{O}_2$ which is seen to act as a catalyst for this degradation and quicken its progress. In any case, it is of greater benefit to produce superconducting films without the need for post-annealing for quicker turnaround in experimental work.

5.3 Josephson Junction Characterisation

Once fabrication of a superconducting trilayer is successful, the next crucial step will be characterising the quality of the junctions produced. JJs are typically characterised by their current-voltage characteristics or $I_c(\Phi)$ modulation.

5.3.1 Current-Voltage Characteristics

There are four parameters that define most of the I-V characteristics of JJs; the gap voltage ($V_{gap}$), the normal resistance ($R_N$), the critical current ($I_C$), and the subgap resistance ($R_{sg}$). All of these values are visualised on the graph in Fig. 56.

1. **Gap Voltage**: As $V_{gap}$ is directly related to the energy gap $2\Delta$, it reflects the superconducting properties of the Nb electrodes. The energy gap and critical temperature of superconducting electrodes of thickness $<\lambda_L$, will be significantly decreased compared to bulk Nb. Therefore, it follows that the thicker the films, the higher $V_{gap}$ and the higher the quality of the film will be. $V_{gap}$ can also be affected by impurities in the
fabrication process. Values of $V_{\text{gap}} > 2.8mV$ at $T = 4.2K$ indicate a very high junction quality.\(^{191}\)

2. **The $I_C R_N$ Product**: $I_C$ scales with JJ geometry whilst $R_N$ scales inversely. Hence the product of these is invariant. From BCS theory, the temperature dependence of the $I_C R_N$ can be calculated as\(^{192}\)

$$I_C R_N = \frac{2\Delta}{4e} \tanh \frac{2\Delta}{4k_B T}$$

(76)

This expression describes ideal Cooper pair tunnelling which considers the tunnelling layer as a rectangular potential barrier. In reality, the barrier varies in all 3 dimensions. However, the measured $I_C R_N$ can be a useful parameter for determining the Cooper pair strength in a real JJ. Experimentally measured values of $I_C R_N > 1.5mV$\(^{191}\) indicate a good tunnelling barrier. To come close the ideal tunneling described above, the barrier should be well-defined, meaning that it is homogeneous in space and has no impurities.

3. $R_{\text{sg}}/R_N$: $R_{\text{sg}}$ is the resistance regime that is observed below the superconducting energy gap. $R_{\text{sg}}/R_N$ is a junction geometry independent quantity and allows comparison between all junctions made from the same material. Junctions with $R_{\text{sg}}/R_N > 10$ at 4.2 K are considered generally good quality junctions.\(^{191}\)

The $I_C R_N$ product and $R_{\text{sg}}/R_N$ can be combined into one junction geometry independent parameter, the characteristic voltage $V_m$:

$$V_m = I_C R_{\text{sg}}$$

(77)

$V_m > 30mV$ is indicative of a high quality junction\(^{191}\)

Figure 56: I-V Characteristics of a Josephson Junction. Adapted from Kaiser (2014).\(^{191}\)
5.3.2 \( I_C(\Phi) \) Modulation

\( I_C(\Phi) \) modulation involves applying a magnetic field to a JJ and measuring the modulation of the flux or current. \( \mathbf{B} \) can penetrate the insulating barrier of thickness \( t_{ox} \) and the adjacent superconducting electrodes to a distance \( \lambda_L \) from the barrier. The magnetic flux penetrating the junction is thus \( \Phi = \vec{B} d(t_{ox} + 2\lambda_L) \). \( I_C(\Phi) \) modulation is given as the absolute value of the Fourier transform of the integral critical current density \( \Upsilon_C(x) \). For an ideal rectangular shaped JJ\(^{\text{xiii}}\), the Fourier transform can be calculated analytically\(^{\text{B}}\) and is given by

\[
I_C(\Phi) = I_c \left| \sin \left( \frac{\pi \Phi}{\Phi_0} \right) \right| \tag{78}
\]

The data should fit an expected Fraunhofer pattern as seen in Fig. 57. \( I_C(\Phi) \) measurements are an important tool for the characterization of junction quality. If the obtained \( I_C(\Phi) \) modulation deviates from the expected patterns, the spatial critical current distribution \( j_c(x, y) \) differs from the expected behaviour. This is indicative of a tunnelling barrier with varying spatial thickness or imperfections in the fabrication process.

Figure 57: Simulation of \( I_C(\Phi) \) modulation for a square junction. Adapted from Kaiser (2014).\(^{191}\)

\(^{\text{xiii}}\) A similar function exists for circular junctions but involves the inclusion of Bessel functions. For more information see Kaiser (2014)\(^{191}\) Chapter 3.
5.3.3 Shielding

JJs are extremely susceptible to external magnetic fields, noise induced by voltage step transitions and small temperature fluctuations. As a result, external shielding is generally required in order to perform successful measurements. Shields are typically made of a type-I superconductor, in some cases Al ($T_C = 1.18\,K$)\(^{193}\). Unlike ferromagnetic materials, however, the magnetic shielding efficiency of superconductors depends on the path of the shielding current loops, hence many shields take the shape of a cylinder\(^{194}\). MuMetal (nickel–iron soft ferromagnetic alloy) has also be utilised\(^{195}\).

However, Yu et al.\(^{196}\) published electronic measurements of internally shunted JJs where no attempt was made to shield the JJs from external magnetic fields. Despite the lack of shielding, sufficiently high $I_C (12.5\,mA)$ and $I_C R_N (0.63\,mV)$ values to make the junctions suitable for practical applications were recorded.

![Figure 58: I–V characteristics of a typical $5\,\mu m \times 5\,\mu m$ junction with a $10\,nm$ thick barrier at 4.2, 7, and 10 $K$. The inset shows the results of the $I_C(\Phi)$ modulation. Adapted from Yu (2006).](image)

Fabrication of a custom built setup for JJ measurements could be a costly affair. Alternatively, it may be easier to utilize the measurement facilities in Karlsruhe Institute of Technology (KIT), Germany as the APRG have connections with the KIT Superconducting Metamaterials Group although this brings up new issues regarding time and turnover of samples. There must be serious consideration of either approach before moving forward.
Bibliography

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3 H Kamerlingh Onnes. Further experiments with liquid helium g. on the electrical resistance of pure metals etc. vi. on the sudden change in the rate at which the resistance of mercury disappears. Koninklijke Nederlandse Akademie van Wetenschappen Proceedings Series B Physical Sciences, 14:818–821, 1912.


Appendices
A  Graphs of the rate of change of resistance with respect to temperature

Figure 59: dR/dT vs Temperature for the deposited films. For the samples B and C, there is a more drastic fluctuation around the transition temperature, possibly owing to their reduced thickness. The minimum in Fig. 59a and the maximum in Fig. 59b correspond to $T_c$.
B Residual Resistivity Ratio

In the case of a thin film where thickness and sheet resistance are known, \( \rho = R_Sd \). The ratio of the resistivities will be the ratio of the sheet resistance at room temperature and before transition. The residual resistivity ratios were found using the following values:

<table>
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<tr>
<th>Sample</th>
<th>Sample C</th>
<th>Sample D</th>
<th>Sample E</th>
<th>Sample F</th>
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<tr>
<td>( d ) (nm)</td>
<td>10</td>
<td>11.5</td>
<td>25.2</td>
<td>35.1</td>
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<tr>
<td>( T_{BT} ) (K)</td>
<td>6.364</td>
<td>5.785</td>
<td>7.683</td>
<td>7.713</td>
</tr>
<tr>
<td>( R_{300K} ) (( \Omega ))</td>
<td>32.42</td>
<td>33.9725</td>
<td>7.9524</td>
<td>4.09945</td>
</tr>
<tr>
<td>( R_{T_{BT}} ) (( \Omega ))</td>
<td>11.663</td>
<td>17.9115</td>
<td>3.02455</td>
<td>1.023</td>
</tr>
</tbody>
</table>

Table 7: Resistance values at room temperature and the transition temperature. \( \Delta T_c \pm 0.001K, \Delta d = \pm 0.1nm, \Delta R = \pm 1 \times 10^{-5} \Omega \)

The associated error for RRR is found by standard error propagation methods:

\[
\delta f = \left( \frac{\partial f}{\partial x} \right)^2 \delta x^2 + \left( \frac{\partial f}{\partial y} \right)^2 \delta y^2
\]

\[
\Delta \rho^2 = d^2 \Delta d^2 + R_i^2 \Delta R_j^2
\]

\[
\Delta RRR^2 = \left( \frac{1}{\rho_{T_{BT}}} \right)^2 \Delta \rho_{300K}^2 + \left( \frac{\rho_{300K}}{\rho_{T_{BT}}^2} \right)^2 \Delta \rho_{T_{BT}}^2
\]
C Preparation of a Stepped Surface

C.1 Introduction and Motivation

C.1.1 Faceting

As previously mentioned in Section 1.2.9, faceting is the process of the decomposition of a surface into two or more planar surfaces. The formation of facets on the c-plane $\alpha$-Al$_2$O$_3$ begins with the creation of 0.2 nm high steps. These steps prefer to exist in pairs. The pairs then bunch together and form facets. These facets are typically multiples of 1.3 nm in height.\(^{197}\)

A comprehensive model to explain faceting does not yet exist. At the size regime of faceting, the structural evolution of the surface involves collective behaviour that is strongly influenced by finite size effects that occur at the atomic scale. A model described by continuum mechanics or one based on the individual behaviour of atoms alone will not sufficiently describe the phenomenon. The formation of facets on solid surfaces is often discussed in terms of the equilibrium crystal shape (ECS) of small crystalline particles.\(^{198,199}\) The ECS is obtained when the total surface free energy $\int \gamma A$ (where $\gamma$ is the surface energy density and $A$ is the surface area) is minimized. For an isotropic material, $\gamma$ is constant so the ECS is a sphere. For an anisotropic 3D crystal, each facet has a surface energy that is orientation dependent. Faces with a lower surface energy form preferentially. Marchenko proposed a model where the strain at the interface between facets is unbalanced causing elastic forces to form which propagate into the bulk.\(^{200}\) These structures exhibit an optimum period that corresponds to the minimum of the surface free energy. Other models suggest that faceting transitions occur as the result of competing free energy curves induced by surface composition changes due to impurity adsorption.\(^{201,202}\)

Faceting on Al$_2$O$_3$ surfaces is dependent on a variety of annealing parameters. An investigation by Pham Van et al.\(^{203}\) demonstrated a proportional relationship between step height and temperature dependence.\(^{203}\) In a study by Ribič et al. $\alpha$-Al$_2$O$_3$ was annealed for 16 hours at 1500°C and step bunching was observed.\(^{204}\) Other factors such as annealing environment and pressure of anneal have also been probed.

The step periodicity as a function of annealing temperature has also been studied in the aforementioned Ribič study and by the APRG\(^{205}\) among others. It can be seen that it will increase with annealing temperature. This faceting mechanism can be considered to be a thermally activated diffusion process. The periodicity of the steps is equivalent to the average adatom displacement, $D$.\(^{206}\) The relationship between adatom displacement and temperature can be given by the Einstein equation

$$D = D_0 e^{-E_{ac}/k_B T} \quad (79)$$

where $E_{ac}$ is the activation energy. In addition to temperature, most studies agree that increasing the annealing time will increase the periodicity to a saturation point, after which further annealing time has little effect.\(^{207}\)
Work previously undertaken by Dr O. Ualibek of the APRG investigated the morphology of c-plane Al$_2$O$_3$ after annealing in the range of 1350°C to 1550 °C for 15 hours.[46] AFM scans of one such surface from this work can be seen in Fig. 60.

![AFM scans of c-plane Al$_2$O$_3$](image)

Figure 60: c-plane Al$_2$O$_3$ annealed for 15 hours at 1400°C. The surface is miscut in the [1210] direction. The inset (B) shows the line profile of the surface indicating a uniform surface with periodicity $100 \pm 17 \text{nm}$. The 3D profile in (C) shows a periodic arrangement of alternating facets. Adapted from Ualibek (2015).[50]

C.2 Annealing of Al$_2$O$_3$

Four separate 1cm$^2$ substrates of various planes of Al$_2$O$_3$ were prepared in this section of the study; two m-plane (1010), one r-plane (1102) and one c-plane (0001). All four substrates were sonicated first in acetone and then IPA for 15 minutes each to remove photoresist and any other contaminants.

The substrates were each annealed separately. Following the preparation of a substrate, it was placed in the ceramic boat seen in Fig 61. The boat was then placed in the GLS-1600X and manoeuvred towards the centre of the tube to ensure the substrate was exposed to the highest heat possible.
The first m-plane substrate was annealed under the following recipe:

1. Increase temperature $T$ from 50°C to 1550°C over a period of 300 minutes.

2. Anneal the substrate for 24 hours.

3. Reduce $T$ from 1550°C to 50°C and remove the substrate.

Atomic force microscope (AFM) scans of the first m-plane Al$_2$O$_3$ annealed surface are presented in Fig. 62a and Fig. 62b.

From Fig. 62b, it can be seen that faceting has occurred on the surface although not in the desired step-and-terrace configuration. There is a lack of order in the facets that have formed and a complete lack of periodicity between the steps that have formed. The step height is around the desired range ($\leq 5\,nm$) however, the terrace widths are on the order of $\sim 100\,nm$. 
whereas the desired widths are on the order of hundreds of nanometres. Unbeknownst to the team at the time, the thermocouple was not functioning properly so the real temperature of the anneal was likely much lower than required. However, it was assumed that the furnace was working as expected and so an alternative second recipe was adopted for the remaining substrates. The remaining three substrates were annealed under the following recipe:

1. Increase $T$ from 50°C to 750°C over a period of 90 minutes.
2. Anneal the substrate at 750°C for 60 minutes.
3. Increase $T$ from 750°C to 1400°C over a period of 180 minutes.
4. Anneal the substrate for 24 hours.
5. Reduce the temperature from 1550°C to 750°C over a period of 180 minutes and remove the substrate.

AFM scans of the remaining m-plane, c-plane and r-plane Al$_2$O$_3$ substrates were also taken. The scans and their corresponding lineshapes can be seen in Figs. 63, 64 and 65.

Figure 63: AFM data of m plane sapphire sample annealed at 1400°C for 24 hours. This 5×5 µm scan was captured with a resolution of 256×256 px.

Despite the extended annealing time and additional annealing at lower temperatures, faceting was not observed on any of the surfaces. This is particularly unexpected as the recipe followed for these samples closely adheres to a recipe used by Dr. B O’Dowd, which resulted in well-ordered array of steps and terraces with an average periodicity of 120 nm. Prior to loading these samples, it was noticed that the furnace was not heating as expected. Upon further inspection, it was discovered one of the SiC heating elements surrounding the tube had cracked. This may have been a result of previous anneal of 1550°C which pushed the system to its maximum working temperature. A replacement rod was installed, however there was still a fault with the thermocouple that went unnoticed that affected the anneal. At this point in the study, ICP etching was considered as an alternative to annealing to produce a stepped surface.
Figure 64: AFM data of c-plane Al₂O₃ annealed at 1400°. This 1×1 μm scan was captured with a resolution of 2048×2048 px.

Figure 65: AFM data of r-plane Al₂O₃ annealed at 1400°. This 1×1 μm scan was captured with a resolution of 2048×2048 px.
C.3 ICP Etching of Substrates

$\text{Al}_2\text{O}_3$ is known as a very hard material which is difficult to remove by RIE. To combat this, a Si (100) substrate was used in the etch instead. An ICP etch tends to be very isotropic. To prepare the substrate for the etch, a photoresist mask was used to prevent etching in a desired direction. The substrate was sonicated with IPA and acetone before being removed and heated on a hotplate. Following heating, the photoresist was spun on the sample. This is done by pipetting a small amount of photoresist on the surface of the substrate before placing it on a spin coater. The substrate is then spun so that the photoresist can cover the entire surface and any excess photoresist is removed. Following this, the substrate was exposed to UV light. Only half of the substrate was exposed to UV light in order to achieve the desired step and terrace configuration. Once exposed to UV, the photoresist is able to dissolve in photoresist developer.

Two Si(100) samples were prepared for ICP etching. One was etched for 120 seconds and the other for 60 seconds. Both were etched in an $\text{SF}_6/\text{CH}_4$ mixture. The AFM scan and line profile of both ICP etched Si (100) samples are seen in Fig. 66 and Fig. 67. From both Fig. 66b and Fig. 67b, clearly defined step heights of $\sim 60 \text{nm}$ and $\sim 200 \text{nm}$ can be seen, greatly outside of the desired range ($\leq 5 \text{nm}$).

![AFM of Si (100) Topography](a) AFM of Si (100) Topography

![Lineshape of Si Surface](b) Lineshape of Si Surface

Figure 66: AFM data of ICP Etched Si(100) for 60 seconds. This 1x1 $\mu$m scan was captured with a resolution of 256x256 px.

![AFM of Si Topography](a) AFM of Si Topography

![Lineshape of Si Surface](b) Lineshape of Si Surface

Figure 67: AFM data of Si ICP etched for 2 mins. This 10x10 $\mu$m scan was captured with a resolution of 1024x1024 px.
Controlling the etch at this scale is not as easy as just reducing the time spent under etching. Etching on the nanoscale is fundamentally more difficult for two basic reasons: a) there is greater difficulty in transporting neutral species in and out of smaller features and b) as the sidewalls get closer together there will be an increased effect of charging by ions and electrons. Improvements in masking and ICP technology have enabled sub-10nm features to be patterned but there are other issues associated with this such as reduced selectivity over the mask and damage to the profile. At this juncture, ICP etching was abandoned in favour of other alternatives.

### C.4 Abandoned alternatives

Ion milling is a physical etching technique performed in vacuum where ions of an inert gas (in this case argon) from a wide beam ion source are accelerated towards the surface of a substrate. These high energy ions bombard the surface removing the loosely bounded surface atoms in order to remove material to some desired depth. This was attempted on a substrate of c-plane Al$_2$O$_3$. The AFM scans of this substrate show no removal of material from the surface. This arises from the aforementioned hardness of Al$_2$O$_3$ making it a poor candidate for this type of etching. This method was also abandoned.

![AFM data of Ar Ion etched c-plane Al$_2$O$_3$](image)

*Figure 68: AFM data of Ar Ion etched c-plane Al$_2$O$_3$. This 2×2 μm scan was captured with a resolution of 2048×2048 px. This scan was taken around the area where the etch was aimed toward but no step was observed likely due to the hardness of the Al$_2$O$_3$ surface.*

It is clear from the above, that fabrication of an ordered stepped surface is a challenging hurdle to overcome. The best method will facilitate a high level of control at sub-5nm feature size which is difficult to achieve. As the project developed, it was decided that the idea of utilizing the step as a barrier layer would be retired and focus would be placed on developing a novel crystalline barrier for the junction.
Figure 69: XPS Spectrum of C 1s Peak prior to anneal. Presence of single and double bonded carbon oxides is observed.
Figure 70: XPS Spectrum of O 1s Peak prior to anneal. Potentially Nb$_2$O$_3$ is present around 530.1 eV. 

Figure 70: XPS Spectrum of O 1s Peak prior to anneal. Potentially Nb$_2$O$_3$ is present around 530.1 eV.
E  XPS Spectra of C Content post 2 hour 700°C anneal

Figure 71: XPS Spectrum of C 1s Peak post 1st anneal. Initially, the NbC peak was mis-attributed as the C-C peak causing a shift in binding energies for all spectra post anneal. It was later realised that the FWHM of the true C-C peak was more in line with those of other C-C peaks found in the course of this study. As a general rule of fitting, parameters such as the FWHM don't change massively between components. The NbC peak was attributed to 282.8 eV.  

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F Survey Scan, Nb and C Content following two weeks in vacuum

Figure 72: Survey scan of Nb-22 following two weeks under vacuum. There is an increase in C content.
Figure 73: XPS Spectrum of Nb 3d Peak following two weeks under vacuum. No significant changes are observed. Deviations from Fig. 33 are likely fitting errors.
Figure 74: XPS Spectrum of C 1s Peak following two weeks under vacuum. An increase in the amount of adventitious C is noted. The unusual increase of adventitious C may be due to other users of the system introducing C when transferring samples.
Figure 75: XPS Spectrum of C 1s Peak following 2\textsuperscript{nd} anneal. It would seem that NbC accounts for the entire spectrum.
H Survey Scan, Nb and C Content following two weeks in vacuum (second round)

Figure 76: Survey scan of Nb-22 following two weeks under vacuum.
Figure 77: XPS Spectrum of Nb 3d Peak following two weeks under vacuum.
Figure 78: XPS Spectrum of C 1s Peak following two weeks under vacuum. An increase in the amount of adventitious C is possibly due to other users of the system introducing new samples into the XPS chamber.
I Survey Scan and Nb Content post 16 hour 680°C anneal

Figure 79: Survey Scan of Nb-22 post 3rd anneal.
Figure 80: XPS Spectrum of Nb 3d Peak post 3$^{rd}$ anneal.
## J LEED Parameters

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Table 8: Parameters for first set of LEED images

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Table 10: Parameters for third set of LEED images