Superconducting NbN thin films for use in superconducting radio frequency cavities

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Abstract

In recent years, renewed interest has been given to alternatives to bulk Nb for use in superconducting radio frequency (SRF) cavities. Much of this research has involved the use of thin films of Nb or other alternative high $T_c$ materials. Given the recent insights into the potential of single layer high $-\kappa$ materials and the prospective performance improvements due to the use of multilayer (ML) superconductor–insulator–superconductor (SIS) film structures, NbN stands as a potential candidate for use in future accelerating cavities. Much of the research completed thus far has focused on the deposition of NbN onto single crystal substrates such as Si and MgO, or onto bulk Nb. In this study, the deposition of high $T_c$ NbN thin films onto copper substrates, in the form of both single layers and as part of an ML SIS structure, using DC magnetron sputtering (DC MS) was explored. The effects of the deposition parameters on the film microstructure and superconducting properties of the NbN films as well as the challenges involved in depositing ML SIS films onto copper substrates are reported on. A maximum $T_c = 16.1$ K has been achieved for single layer NbN films, as determined by AC susceptometry measurements. Initial results for the SIS film structures, deposited onto copper in the form of Nb/AlN/NbN, have also shown an enhancement in the first magnetic flux entry field value above that achieved by a single Nb layer. This enhancement has been found to be highly dependent on the quality of the SIS film coatings.

Keywords: SRF cavity, NbN thin film, coated copper, SIS coating, critical temperature, first magnetic flux entry field

(Some figures may appear in colour only in the online journal)

1. Introduction

The pursuit of improved performance and decreased costs has led to increased interest in alternative approaches to superconducting radio frequency (SRF) cavity manufacture. Alternative materials and methodologies to the current standard of bulk Nb are being explored. The potential use of high-$-\kappa$ materials, which are materials with a large ratio of the penetration depth to the coherence length, has found renewed interest due to recent insights regarding vortex nucleation [1]. The use of alternative multilayer (ML) superconductor–insulator–superconductor (SIS) structures has also been investigated, in order to increase the penetration field into bulk superconductors above their theoretical limit [2, 3]. The results from studies into the use of these ML SIS structures have already shown the potential for delayed vortex penetration [4–6].

There are a number of potential materials to be considered for these applications [7]. One of these materials, namely NbN, is an ideal candidate due to its high superconducting transition temperature $T_c = 17.3$ K, already achieved through sputtering [8], its high critical field $H_c = 230$ mT [9] and its relative ease of manufacture. Until now, much of the research into the deposition of NbN thin films was completed using single crystal substrates, such as Si and MgO, or bulk Nb.
The superconducting properties of NbN are strongly dependent on the formation of the correct crystallographic phase. NbN forms in three superconducting phases, with \( T_c \)'s ranging from 11.6 K for the hexagonal \( \epsilon \)-phase [10], 12–15 K for the tetragonal \( \gamma \)-phase [11] and up to 17.3 K for the cubic \( \delta \)-phase [8]. All other phases are non-superconducting and include the hexagonal \( \beta \) (NbN\(_2\)), \( \delta' \) (NbN) and further higher order nitrides such as Nb\(_2\)N\(_3\) and Nb\(_3\)N\(_6\) [12]. The phases of Nb\(_n\) exist in different Nb:N ratios, detailed as follows [13]: (a) \( \delta \)-Nb\(_2\)N, \( x = 0.4-0.5 \), (b) \( \gamma \)-Nb\(_2\)N\(_3\), \( x = 0.75-0.8 \), (c) \( \delta \)-NbN, \( x = 0.88-0.98 \) and 1.015–1.062, (d) \( \epsilon \)-NbN, \( x = 0.92-1 \), (e) \( \delta' \)-NbN, \( x = 0.96 \). Therefore, in order to ensure the correct stoichiometry of the films and the subsequent synthesis of the \( \delta \)-NbN phase, the deposition parameters play an integral role. Two of the most critical deposition parameters are the nitrogen percentage [14], and the process pressure [15]. A first indication of crystallographic phase formation is provided by the colouring of the film. A gold film is indicative of the cubic (\( \delta \)) or tetragonal (\( \gamma \)) NbN phase while a silver colour is indicative of the hexagonal phases of NbN [16]. The lattice constant of NbN films is often used as an indication of the stoichiometry and vacancy content of the films. Superior film properties have been associated to films with bulk-like lattice parameter values (\( a = 4.378-4.42 \) Å) [17].

One known issue with NbN films is their early flux penetration values. In relation to this, the effects of nano-scale surface topography of high-\( \kappa \) materials have also been investigated, with the results hinting at a possible explanation for the early flux penetration in NbN films [18]. Increased surface roughness has also been linked to increased flux pinning. However, the scale of surface roughness responsible for flux pinning is associated with the applied field, where high fields are more sensitive to smaller-scale roughness [19]. To counteract this issue, NbN films deposited with thicknesses less than the penetration depth, have also been shown to have enhanced lower critical field values at lower thicknesses [20].

The sought after shielding effect purported to be provided by SIS structures requires the deposition of superconducting films with thicknesses less than their penetration depth. Theoretical predictions for the optimum thicknesses of the insulating and the outer superconducting layer in ML SIS structures for both ‘clean’ (defect free) and ‘dirty’ (defect affected) films have been concluded [21, 22]. NbN has already been used successfully in the development of SIS structures found in Josephson Junctions [15], which points to their potential in SRF cavities. There are a number of potential materials which can be used as insulating layers in SIS structures, such as MgO, Al\(_2\)O\(_3\) and AlN. However, in the event of depositing Al\(_2\)O\(_3\) or MgO as the insulating layer, exposure of the already deposited Nb layer and the Nb target itself to oxygen, is concerning, given the effects of oxygen on the superconducting properties of Nb [23]. The \( \langle 002 \rangle \) AlN phase also exhibits a low lattice mismatch with \( \langle 111 \rangle \) NbN [24], thereby facilitating its growth in the final superconducting layer. AlN has also been found to increase the \( T_c \) of NbN films, specifically very thin NbN films [25]. As such, AlN was chosen as the material for the insulating layer in this study.

In this paper, the results of optimised NbN thin films, typically 1.2 \( \mu \)m thick, on polycrystalline copper substrates as well as initial results for NbN-based ML SIS films of the form: Cu substrate/Nb/AlN/NbN are reported on. Films were also simultaneously deposited onto Si witness samples for use in microstructural analysis. The study focused on optimising the films for high \( T_c \) values and as such, the effects of changing deposition parameters on the film microstructure and subsequent superconducting properties are detailed.

2. Experimental

The NbN thin films and the ML SIS films were deposited onto electropolished OFHC copper substrates, as well as Si witness samples, via reactive DC magnetron sputtering (DC MS) with a fixed target to substrate distance of 5.5 cm. The films were deposited using a 100 \( \times \) 100 mm\(^2\) Nb (RRR 300) target in a commercial, high-volume, fully automated coating system (CemeCon CC800) with a base pressure of 5.0 \( \times \) 10\(^{-7}\) mbar. Based on the results of previous studies [26], the films were deposited using a mixture of argon (99.999 Vol%) and nitrogen (99.999 Vol%) gases. The \( \text{N}_2/\text{Ar} \) ratio was maintained via flow rate control of the two gases. Prior to deposition, the system, including the substrates, was passively baked at 280 °C for 6 h. Following this, the substrates were subjected to a medium frequency etching process as a final surface treatment and the Nb target was sputter cleaned for 10 min to ensure all possible contaminants were removed.

From initial experiments, it was discovered that a high cathode power and low deposition pressure leads to the deposition of higher density films [26]. To further understand this, a first series of NbN films were deposited at a fixed pressure of 8.0 \( \times \) 10\(^{-3}\) mbar, at individual \( \text{N}_2 \) flow rates ranging from 6%–30% of the total Ar and \( \text{N}_2 \) flow rates. A second series of films were deposited with a constant 10% \( \text{N}_2 \) flow rate, at individual deposition pressures ranging from 8.0 \( \times \) 10\(^{-3}\) to 1.8 \( \times \) 10\(^{-2}\) mbar. These results were later utilised to optimise the parameters for the deposition of high \( T_c \) single phase \( \delta \)-NbN.

The ML SIS films, arranged in the order Cu-substrate/Nb/AlN/NbN, utilised a three step coating process with a 2 h temperature stabilisation period in between the separate coatings. The thickness of the Nb base layer and the insulating AlN layer were maintained at 4 \( \mu \)m and 30 nm respectively, while the NbN layer was deposited in thicknesses of 150 nm, 200 nm and 250 nm, in order to investigate the effects of the outer superconducting layer thickness on SIS film performance. The deposition parameters are summarised in table 1.

Microstructural analysis of the films was completed using a Zeiss Ultra 55 scanning electron microscope (SEM). Silicon witness samples were cleaved in order to determine the thickness of each film and to examine their cross-sectional structure. The presence of any contaminants was simultaneously determined using an energy-dispersive x-ray detector attached to the SEM. The surface morphology of the samples was
examined with a Haloycns XE-100 atomic force microscope (AFM) in non-contact mode, with a scan size of $5 \times 5 \, \mu m^2$ as well as an Olympus LEXT OLS 4000 confocal laser scanning microscope (CLSM) with a scan size of $257 \times 257 \, \mu m^2$.

The crystallographic characteristics of the films were determined using x-ray diffraction (XRD) (Panalytical Empyr-ean diffractometer with a Cu $K\alpha$ source) utilising $\theta - 2\theta$ Bragg–Brentano scans, which also assisted with phase identification. The average crystallite sizes of all samples were calculated using the Scherrer equation while the lattice parameters were determined using the Bragg equation. The instrumental broadening was accounted for by the use of a lanthanum hexaboride standard sample. The results of the XRD scans were correlated with the results from a previous Rutherford backscattering (RBS) analysis, which provided the Nb:N ratio in the films as a result of different levels of N$_2$% in the deposition gas [26]. This allowed for accurate discernment of the NbN phases.

Sections of these same samples were used in DC magnetisation studies to investigate the basic superconducting properties. Small samples of approximately $2 \times 2 \, mm^2$ were tested using a vibrating sample magnetometer (VSM) option of the commercial physical property measurement system (PPMS) system—Model 6000, from Quantum Design Inc. Two superconducting characteristics of the samples were determined: the critical temperature ($T_c$) and the first magnetic flux entry field, denoted shortly as the ‘entry field’ ($H_{\text{en}}$). The DC magnetisation curves of the samples were measured at constant temperature 4.2 K, after the cool-down below DC magnetisation curves of the samples were measured at constant temperature 4.2 K, after the cool-down below DC magnetisation curves of the samples were measured at constant temperature 4.2 K, after the cool-down below DC magnetisation curves of the samples were measured at constant temperature 4.2 K, after the cool-down below

| Parameter            | Range          | Unit |
|----------------------|----------------|------|
| Cathode power        | 400–500        | W    |
| Derived power density| 4–5            | W cm$^{-2}$ |
| Temperature          | 260–280        | °C   |
| Process pressure     | (0.6–1.8) $\times 10^{-2}$ | Mbar |
| $N_2/(Ar + N_2)$ flow ratio | 6–30        | %    |

With the main goal of the study being to compare the performance of the individual thin film samples with each other, small sections of the samples of almost identical dimensions were prepared for the VSM measurements. No correction for the geometrical effects was completed when evaluating the entry field. As described above, the reported $H_{\text{en}}$ values consider the applied field but are smaller than the actual physical first magnetic flux entry field values experienced at the sample surface.

A certain estimate of the geometrical field enhancement factor can be made on the basis of analytical study completed by Chen et al [27], where an infinitely long rectangular bar in a transversely applied field, representing an idealised 2D approximation of the VSM sample geometry was considered. For our typical sample dimensions (aspect ratio ~0.002) these results show that the field on the top surface (sample face) is practically equal to $H_{\text{en}}$, while on the side surface of the sample (the edge perpendicular to $H_z$), the field reaches 2 $H_{\text{en}}$ within a distance of approximately $0.025 \times$ film thickness from the edge, increasing towards the sample edge. One could thus estimate the geometrical field enhancement factor to be approximately 2 for the samples considered in this study.

In the DC magnetisation studies, the critical temperatures have been determined from the temperature dependence of the magnetic moment in a constant applied magnetic field of 5 mT, parallel to the sample flat face. The magnetic moment was measured while monotonically decreasing the temperature from 20 K to 5 K in 0.05 K steps. The superconducting transition (critical) temperature $T_c$ was taken as the onset of the magnetic moment change. In the case of the ML SIS samples, the applied 5 mT DC magnetic field was found to be too high to detect the superconducting transition of the thin NbN layer and only the transition of the much thicker Nb layer was clearly visible. In order to increase the sensitivity of the critical temperature measurement, the highest performing samples were also tested using the AC susceptometer option of the PPMS. In these measurements, an AC magnetic field with the amplitude of 0.02 mT and frequency of 42 Hz was applied perpendicular to the flat sample face. While decreasing the temperature from 20 K to 5 K in steps of 0.1 K, the real ($m_r$) and imaginary ($m_i$) parts of the first harmonic component of the sample’s magnetic moment were measured. Similar to the DC measurements, the $T_c$ was determined as the onset of the $m_r$ change with decreasing temperature.

3. Results and discussion

3.1. NbN single layer films—nitrogen percentage effects

Initial experiments sought to optimise the $\delta$-NbN phase by adjusting the $N_2/(Ar + N_2)$ ratio from 6% to 30%. A cathode power of 500 W and a deposition pressure of $8 \times 10^{-3} \, \text{mbar}$ were maintained to ensure the deposition of films with a dense microstructure, as previous studies showed [26]. The films display a dense cross-sectional microstructure, regardless of the level of N$_2$ content in the process gas. There is also no evidence of voids between the film and the substrate, nor any evidence of film delamination. As detailed in figures 1(a) and (b), films

Table 1. NbN deposition parameter windows.

| Parameter          | Range    | Unit |
|--------------------|----------|------|
| Cathode power      | 400–500  | W    |
| Derived power density| 4–5     | W cm$^{-2}$ |
| Temperature        | 260–280  | °C   |
| Process pressure   | (0.6–1.8) $\times 10^{-2}$ | Mbar |
| $N_2/(Ar + N_2)$ flow ratio | 6–30 | %    |
Figure 1. SEM images of samples deposited at 500 W cathode power and at a deposition pressure of $8 \times 10^{-3}$ mbar. The images of the cross section are films deposited on Si while the surface images are films deposited on Cu. (a) and (b) display the 8% N$_2$ sample and (c) and (d) display the 18% N$_2$.

Figure 2. XRD patterns of Nb$_x$N$_y$ on Cu samples deposited at different nitrogen to argon ratios, denoted as nitrogen percentages next to the respective scan. The spectra are plotted in log scale.

Figure 3. (a) Plot detailing the change in the lattice parameter and the average $\delta$-NbN (111) crystallite size, with increasing N$_2$ percentage. (b) Plot detailing the change in critical temperature and entry field in parallel field, with increasing N$_2$ percentage.

This surface structure is similar for all films deposited in this series, regardless of N$_2$ content. As such, the average surface roughness of these samples is $S_q = 8.19 \pm 3.68$ nm as measured by AFM.

Two of these samples, those deposited at 6% and 8% N$_2$ respectively, displayed gold coloured films, which indicates the formation of the tetragonal $\gamma$-NbN or cubic $\delta$-NbN phase. The remaining samples displayed silver coloured films, which in this case is indicative of multiphase films. These results were confirmed by the XRD scans displayed in figure 2.

The $\delta$-NbN phase is identified by the peaks at 35.35$^\circ$ and 41.05$^\circ$ [28]. The peaks are fairly broad, indicating a nanocrystalline structure, which correlates with the SEM results shown in figure 1(a). At lower N$_2$ content, samples display a $\delta$-NbN (200)-orientation. An increasing presence of the hexagonal, higher order nitride phase, Nb$_5$N$_6$, as evidenced by the peak at 34.5$^\circ$ [29], is seen with increasing N$_2$/Ar ratios. The relative intensity of the higher order nitride peak surpasses that of the $\delta$-NbN peak above 10% N$_2$. This is understandable, as this phase exists at higher N$_2$ concentrations than the $\delta$-NbN phase. The increase in the hexagonal phase with increasing N$_2$ content was also observed by Havey et al [30], although they observed the $\delta'$-NbN phase.

The changes in the lattice parameter and the average $\delta$-NbN (111) crystallite size, as a function of the N$_2$ content, are detailed in figure 3(a). The entire plot range lies within the values defined for bulk $\delta$-NbN. The lattice parameter is found to increase with increasing N$_2$ content up to a maximum of
4.397 Å at 16% N$_2$, thereafter it steadily decreases with further increase in N$_2$ content. This result is similar to that detailed by Brauer and Kirner [31]. They observed that the lattice parameter reaches a maximum at a ratio of Nb:N $\sim$1. Higher or lower Nb:N ratios lead to a decrease in the lattice parameter due to crystallographic imperfections. This result also correlates well with the RBS analysis results presented for a previous study [26].

The average size of the $\delta$-NbN (111) crystallites display a similar trend to the lattice parameter, increasing to a maximum of 13 nm at 16% N$_2$, where after it decreases. An increase in N$_2$% results in a decreased adatom flux during film deposition which results in an increased surface diffusion time leading to larger crystallites. This is responsible for the initial increase in $\delta$-NbN (111) crystallite size up to $\sim$16% N$_2$. However, further increase in the N$_2$ content leads to an increase in the proportion of the hexagonal Nb$_2$N$_6$ phase. This in turn, results in a decrease in the $\delta$-NbN (111) crystallite size at higher N$_2$ content.

The results of the VSM measurements are displayed in figure 3(b). It is evident that the critical temperatures of these films are fairly consistent, around the 11–12 K mark, besides the sample coated at 6% N$_2$, which displays a specifically low critical temperature. The critical temperature of the 4% and 20% samples could not be accurately discerned from the data at the 5 mT applied field and as such, they were excluded from this figure. The entry field is found to achieve a significant maximum of $H_{en} = 13.0$ mT at 8% N$_2$, falling off at higher and lower values of N$_2$ content. This is related to the formation of non-superconducting hexagonal phases at higher N$_2$ content, as evidenced in the XRD scans, and further non-superconducting phases at lower N$_2$ content.

The generally very low entry fields of the NbN films, a few mT typically, were particularly difficult to determine, mainly due to the small number of data-points measured in the initial linear Meissner trend region. The $m(H_s)$ data-points were recorded at 0.2 mT steps for the virgin curves and as the measured magnetic moment values were correspondingly small in this low $H_s$ region, the experimental noise of the magnetic moment measurement had a stronger impact on $H_{en}$ determination compared to other types of samples. The overall precision of the $H_{en}$ measurement is estimated to be $\pm$2 mT for the NbN samples and approximately $\pm$5% of the value for the other types of thin film samples with higher $H_{en}$ (Nb, SIS) discussed here. In the case of the NbN samples with $H_{en}$ values close to 2 mT, the linear Meissner trend was always visible, however, the reported $H_{en}$ value is only indicative.

3.2. NbN single layer films—deposition pressure effects

A second series of experiments were completed at a constant N$_2$/Ar ratio of 10% N$_2$ and at a high cathode power of 500 W, while adjusting the process pressure from 6.0 $\times$ 10$^{-3}$ to 1.8 $\times$ 10$^{-2}$ mbar. The film colour is observed to change from a silver to a more pronounced gold colour. As described above, the gold colour is indicative of the superconducting cubic phase of NbN becoming evident at deposition pressures $\geq$1.0 $\times$ 10$^{-2}$ mbar.

A similar film structure to that detailed in figures 1(a) and (b) is seen in figures 4(a) and 4(b). This nano-crystalline structure is synonymous with samples deposited at low pressure and with low N$_2$ content. In comparison, films deposited at higher pressures ($>$1.2 $\times$ 10$^{-2}$ mbar) display a pronounced columnar structure, with columns growing from the substrate to the film surface. Additionally, higher deposition pressures lead to a change in the surface topography, with larger, more faceted grains now present on the film surface. This is showcased in figures 4(c) and (d). The presence of voids within the films, often in the form of disjointed columnar crystals, are also more apparent in those deposited at high pressures relative to those deposited at low pressures.

In light of the surface topography changes, AFM and CLSM analysis were conducted on these samples. As shown in figure 5, the increase in the grain size, combined with their faceted nature, leads to a significant increase in the surface roughness. AFM measurements detail $S_q = 4.39 \pm 0.41$ nm at low deposition pressure and $S_q = 21.86 \pm 2.22$ nm at...
high deposition pressure. This effect is more pronounced in the AFM results compared to the CLSM results, due to the different scan sizes employed in each method, detailed in section 2. As a result of this change in scan size, the pixel density of the two methods differs considerably. The CLSM captures images with 15.9 pixels µm\(^{-2}\) while the AFM achieves 10 486 pixels µm\(^{-2}\). As a result of this, the AFM measurements are far more sensitive to any changes in the surface topography, especially at the nanometre scale.

The corresponding XRD results, showcased in figure 6, present predominantly δ-NbN films. However, films transition from a δ-NbN (200) orientation at low deposition pressure towards a pronounced δ-NbN (111) orientation at higher deposition pressure. The presence of the hexagonal δ’-NbN phase, referenced by the peak at \(\sim 34.8^{\circ}\) [32], is also found at pressures ≤1.4 × 10^{-2} mbar.

The evolution of the lattice parameter and the δ-NbN (111) crystallite size, in relation to changing deposition pressure, is presented in figure 7(a). The entire plot range lies within the values defined for bulk δ-NbN. The lattice parameter values display a further reliance on the deposition pressure, increasing up to a maximum of 4.398 Å at 1.4 × 10^{-2} mbar where after they decrease with further increase in pressure. This sample also possessed the highest \(T_c\) in this series, as shown in figure 7(b). The average crystallite sizes are found to increase with increasing deposition pressure, from roughly 6 nm at 6.0 × 10^{-3} mbar to 24 nm at 1.8 × 10^{-2} mbar.

Figure 7(b) shows an increase in the critical temperature with increasing pressure up to a maximum of 15.3 K at 1.4 × 10^{-2} mbar, where after it decreases to 14 K at 1.8 × 10^{-2} mbar. This trend in \(T_c\) vs deposition pressure was shown previously by Bacon et al [33]. Furthermore, the highest \(T_c\) film is constituted by multiple phases, while the single phase δ-NbN film displays a reduced \(T_c\). This is similar to the results obtained by Anderson et al, who found the highest \(T_c\) NbN films always possessed a (111) δ-NbN texture with the presence of a small amount of \(\delta’\)-NbN [34]. On the other hand, the entry field is seen to peak at 8.4 mT at a pressure of 1.0 × 10^{-2} mbar, where after it decreases with further increase in deposition pressure. This decrease in the entry field value is related to the faceted nature of the grain peaks above 1.0 × 10^{-2} mbar. These nano-scale faceted peaks lead to a local field enhancement and the suppression of the superheating field, resulting in early flux penetration [18, 35].

3.3. NbN single layer films—optimised samples

Following these initial investigations, a final series of eight optimised samples were deposited, taking into account the results from the previous samples. The aim with these samples was to maximise the superconducting transition temperature by combining a higher deposition pressure, lower N\(_2\) content and the application of a low bias to maintain a dense film in spite of the increased pressure. All of these samples possessed a gold film colour and columnar growth structure topped by a faceted grain peak on the film surface and achieved an average \(T_c = 14.6 ± 1.1\) K.

Of the final optimised samples, the three best performing samples are presented, referred to here as Opt-1, Opt-2 and Opt-3. Sample Opt-1 was coated at a lower cathode power (400 W), an intermediate deposition pressure (1.2 × 10^{-2} mbar) and a 20 °C higher substrate temperature of 280 °C. This was in an attempt to produce the columnar film found at higher deposition pressures while increasing the film density by enhancing the mobility and surface diffusion of adatoms. A lower N\(_2\) content of 8% was also used to decrease the likelihood of the formation of any non-superconducting hexagonal phases. Similarly, samples Opt-2 and Opt-3 were both coated at 8% N\(_2\) and a substrate temperature of 280 °C. A high cathode power (500 W) and a higher deposition pressure (1.4 × 10^{-2} mbar) were also used with these samples. Finally, sample Opt-3 was deposited with a 75 V substrate bias to further increase surface diffusion and thereby film density. The deposition parameters of these samples, along with their superconducting test and surface roughness results are summarised in table 2.

The microstructure of Opt-3, displayed in figure 8, is similar to that shown in figure 4 and is representative of both Opt-1, and Opt-2 as well. The general columnar nature of the structure has been maintained while the film density has been improved. All samples possess a faceted grain peak, again similar to that seen in figure 4(d), homogeneously deposited across the sample surface. AFM analysis indicates a low RMS surface roughness for all samples, with values of 6.36 ± 0.42, 7.39 ± 2.34 and 14.05 ± 2.32 nm for Opt-1, Opt-2 and Opt-3 respectively.

The XRD scans of the optimised samples, presented in figure 9 indicate a general δ-NbN (111) orientation for the samples. Samples Opt-1 and Opt-3 also display a very low presence of δ’-NbN. The lattice parameter of the samples...
Table 2. Deposition parameters, superconducting test results and AFM surface roughness results for the three highest \( T_c \), optimised NbN thin film samples.

| Sample | Temperature (°C) | Pressure (mbar) | \( N_2\)% | Bias (V) | Power (W) | \( H_{in} \) (mT) | \( T_c \) (K) | \( S_q \) (nm) |
|--------|------------------|------------------|----------|----------|-----------|------------------|------------|------------|
| Opt-1  | 280              | \( 1.2 \times 10^{-2} \) | 8        | 0        | 400       | 2.0             | 15.9      | 6.36 ± 0.42 |
| Opt-2  | 280              | \( 1.4 \times 10^{-2} \) | 8        | 0        | 500       | 2.0             | 15.4      | 7.39 ± 2.34 |
| Opt-3  | 280              | \( 1.4 \times 10^{-2} \) | 8        | 75       | 500       | 5.0             | 16.1      | 14.05 ± 2.32 |

Figure 7. (a) Plot detailing the change in the lattice parameter and the average \( \delta\)-NbN (111) crystallite size, with increasing deposition pressure. (b) Plot detailing the change in the critical temperature and the entry field in parallel field, with increasing deposition pressure.

Figure 8. SEM images of the best performing NbN sample, Opt-3. (a) shows the NbN film cross section on Si and (b) shows the NbN film surface on Cu.

The deposition parameters, as shown in Table 2, were optimised to achieve the maximum critical temperature, \( T_c \). The deposition pressure was varied to investigate its effect on the lattice parameter, crystallite size, critical temperature, and entry field. The results suggest that increasing the deposition pressure leads to a decrease in the lattice parameter and an increase in the crystallite size, as shown in Figure 7. The critical temperature and entry field increase with increasing pressure, consistent with previous reports.

The SEM images in Figure 8 confirm the high-quality surface morphology of the optimised NbN thin films. The film thickness was measured using AFM, and the surface roughness was calculated to be within the desired range for superconducting applications.

Based on the optimised deposition parameters, three samples were selected for further testing. These samples, labelled Opt-1, Opt-2, and Opt-3, were measured using AC susceptibility and X-ray diffraction (XRD) spectroscopy.

The XRD spectra in Figure 9 show the diffraction peaks corresponding to the \( \delta\)-NbN (100), (111), (0002), and (111) phases. The peaks for Opt-1 are sharper and more intense compared to the other samples, indicating a higher degree of crystallinity. The peak at \( 2\theta = 44.6° \) corresponds to the (111) plane, which is characteristic of the \( \delta'\) phase. The presence of this phase in the highest \( T_c \) films corroborates previous observations.

The measured \( m_{re}(T) \) curves, normalised to the \( m_{re} \) value at the low temperature plateau, are displayed in Figure 10. The changes in the deposition parameters for these three samples culminated in the highest critical temperature of all the NbN samples for sample Opt-3 while sample Opt-1 and Opt-2 still displayed a \( T_c > 15 \) K. The presence of the second hexagonal \( \delta'\) phase in the highest \( T_c \) films is similar to what was observed in the deposition pressure samples and previously by Anderson et al. [34].

3.4. NbN-based ML SIS films

Following the successful optimisation of the NbN single layer films, a series of SIS films with a Nb/AlN/NbN structure were also deposited onto OFHC Cu substrates. This structure is shown in Figure 11(a). The AlN recipe was developed as part of
Figure 10. Normalised AC susceptibility results indicating the critical temperature of the three optimised samples.

A separate study, with the final deposition parameters now displayed in Table 3. A separate TEM investigation (not detailed here) showed the crystalline structure of the films while the XRD scans of the resultant AlN film (also not shown here) displayed a (002) orientation, as evidenced by the peak at 36.09° [36].

The SIS film coating was set up in such a way that the sample did not require removal from the deposition chamber in between coatings. The NbN recipe used for the SIS films was based on sample Opt-1. This was chosen before the superconducting measurement data was available. Four SIS film samples (SIS-1, SIS-2, SIS-3, SIS-4) were deposited with NbN thicknesses of 200 nm, 200 nm, 150 nm and 250 nm respectively, based on the work by Kubo [13]. A single DC MS Nb layer was also deposited on a Cu substrate, using the same conditions as the base layer of the SIS film, for the purpose of superconducting performance comparison. A further copper sample was coated with a two-layer Nb/AlN coating for surface roughness evolution studies.

The film thickness homogeneity of the outer insulating and superconducting layers in SIS film structures are important to ensure optimum superconducting performance. As such, the substrate holder was set to rotate during the deposition of the AlN and NbN films in order to avoid a thickness gradient in the film. An initial SIS film trial with a thin Nb layer was completed on a Si (100) sample to better understand the growth of the SIS layers on and to fine tune the process. An SEM image of this film, including layer thicknesses, is displayed in Figure 11(b). It is clear that the NbN layer structure is similar to what was achieved for the single layer NbN sample (Opt-1) that this recipe is derived from. The different films also present a well-connected interface with no visible voided regions.

A focused ion beam (FIB) was used to remove a section of the film on selected SIS samples to better understand their structure. The results for sample SIS-1 are presented in Figure 12(a). It is evident that the interface between the Cu substrate and the Nb film is plagued by voids. Further investigations of the other samples provided evidence of similar interfacial voids as well as partial film delamination. A section of sample SIS-1 was also investigated with TEM. A magnified image of the near-surface ML structure is shown in Figure 12(b). The AlN and NbN layers have a conformal, homogeneous thickness, of ~30 nm and ~200 nm respectively, across the entire surface. The interface between the different material layers is also free of voids. It is also apparent that the Nb film surface is considerably rougher than the underlying Cu surface.

The roughness values, measured by AFM, for the samples coated with SIS films, the pure Nb film, the Nb + AlN film and the single NbN layer film (Opt-1) are shown in Table 4. Of the SIS films, sample SIS-1 has the lowest surface roughness, however the difference between the SIS film samples is small. The results indicate a significantly rougher surface for the SIS films compared to that of the individual NbN layer which they are based on (Opt-1). The single Nb layer sample possesses the highest roughness of all samples, while the Nb/AlN bi-layer possesses a roughness value in between that of the Nb layer and the SIS film. The results point to the noteworthy influence of the Nb layer on the resultant SIS film surface roughness.

Table 3. AlN interlayer deposition parameters.

| Parameter            | Value | Unit |
|----------------------|-------|------|
| Cathode power        | 3500  | W    |
| Derived power density| 6.5   | W cm$^{-2}$ |
| Temperature          | 180   | °C   |
| Process pressure     | $6 \times 10^{-3}$ | mbar |
| Process gas          | N$_2$ (100%) |

Figure 11. (a) Illustration of a multilayer SIS structure to be deposited onto electropolished copper. (b) SEM image of the pre-trial SIS film deposited on Si with a minimal thickness Nb (30 m) base layer.

Figure 12. (a) SEM image showing a FIB cut through full thickness of sample SIS-1 and (b) Magnified TEM image of the multilayer (ML) SIS structure of sample SIS-1.
The XRD spectra for the NbN film, Opt-1, which the SIS films were grown on, indicated a high intensity NbN peak at 34.6° and a secondary NbN peak at 32.6°. The Cu peak was also detected, with a peak at 2θ = 44.6° and 51.6°. The decrease in the Cu peak is due to the increased total thickness of the SIS films, as a result of the increased roughness of the underlying Nb and AlN layers. The AlN peak is indiscernible from the XRD patterns, due to its low relative thickness. The main peak present in the scan of sample Opt-1 was at 2θ = 43.2°. This peak is consistent with what was measured with the single NbN layer film of sample Opt-1. Once more, the film is characterised by a high intensity δ-NbN (111) peak at 35.4° as well as the presence of a secondary δ'-NbN peak at 34.6°. The AIN peak is indiscernible from the XRD patterns, due to its low relative thickness. The main peak present in the scan of sample Opt-1 is that of the Nb layer, identified by the peak at 38.5° [37]. The decrease in the Cu peak is due to the increased total film thickness, as a result of the ~4μm Nb layer.

The critical temperature of the SIS films was also measured using an AC susceptor. The AC susceptor is able to detect the transition of both the underlying Nb layer as well as the outer NbN S-layer. The results for the four SIS films are illustrated in figure 15. The critical temperature of the outer superconducting layer in the SIS films is lower than the single NbN layer with the best performing SIS film (SIS-1) displaying a $T_c = 14.7$ K, compared to $T_c = 15.9$ K for the single NbN layer (Opt-1). This $T_c$ reduction is believed to be due to a combination of reduced film thickness in SIS structures and the increased roughness of the underlying Nb and AIN layers. Further results of the superconducting measurements are also displayed in table 4.

The entry field ($H_{en}$) measurements of the SIS films were also conducted using the VSM. As described above, the sample is immersed in the applied magnetic field $H$, here, both the Cu substrate-to-Nb film interface and the NbN (‘top’) surface of the sample are exposed to the applied field. In this configuration, it seems likely that the signal of the Meissner effect comes mainly from the Nb film, which is approximately 20 times thicker than the NbN top-layer. However, the quality of the Nb surface at the substrate side, predominately in terms of the NbN layer, used in the SIS films, is vastly different to that of the NbN sample used in the SIS films (Opt-1). Therefore, the resultant surface layer structure of the SIS films, and its effectiveness as a shielding layer, is significantly influenced by the underlying Nb layer.

Further inspections of SEM images of the SIS film surfaces, presented in figure 14, indicate a distinct difference between sample SIS-1 and the rest of the samples. Sample SIS-1, figure 14(a), displays a dense, coherent film surface while the rest of the SIS samples, which have a similar surface to figure 14(b), show evidence of gaps between the different grain structures. This can lead to inhomogeneous shielding of the underlying Nb layer and is believed to be due to the heightened roughness of the underlying Nb layer.

The XRD spectra for the NbN film, Opt-1, which the SIS samples utilise, and the best performing SIS film, SIS-1, are shown in figure 9. The results for the NbN layer used in the SIS film are consistent with what was measured with the single NbN layer film of sample Opt-1. Once more, the film is characterised by a high intensity δ-NbN (111) peak at 35.4° as well as the presence of a secondary δ'-NbN peak at 34.6°. The AlN peak is indiscernible from the XRD patterns, due to its low relative thickness. The main peak present in the scan of sample SIS-1 is that of the Nb layer, identified by the peak at 38.5° [37]. The decrease in the Cu peak is due to the increased total film thickness, as a result of the ~4μm Nb layer.

This is further visible when comparing the surface structure of the single layer NbN film with the single layer Nb and SIS film surfaces. The surfaces of the single layer NbN films, presented earlier, consisted of homogeneously deposited surfaces whereas the surfaces of the Nb film, and the subsequently deposited SIS films, present a multitude of different grain structures, as shown in figure 13.

It is evident that the nanoscale NbN grains themselves are still homogeneously grown on the surface of the NbN layer, as shown in figure 14. However, the large scale surface structure of the SIS films is vastly different to that of the NbN sample used in the SIS films (Opt-1). Therefore, the resultant surface layer structure of the SIS films, and its effectiveness as a shielding layer, is significantly influenced by the underlying Nb layer.

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of the surface roughness, is higher than that at the Nb-to-AlN interface and much higher than that of the NbN surface at the NbN-to-vacuum interface. Therefore, the field penetration is believed to start at the NbN-to-vacuum interface, where after the field propagates towards the Nb layer at much smaller applied fields than those required for penetration from the substrate side of the Nb layer. Support for this is found in the considerably different $H_{en}$ values determined for samples SIS-1–4 despite the same Cu substrate and Nb deposition procedure being used for all four samples. Nevertheless, the magnetic moment measured with the VSM originates, predominantly, from the Nb layer. Subtle changes in the measured moment that would indicate field penetration into the NbN layer cannot be realistically detected. The entry field values determined for the SIS samples therefore mark the start of field penetration into the SIS system as a whole.

Samples SIS-2, SIS-3 and SIS-4 display entry field values significantly lower than the individual Nb layer sample. On the other hand, sample SIS-1 has the highest $H_{en} = 64.5$ mT, surpassing the value obtained with the pure Nb sample, $H_{en} = 52.0$ mT. This result indicates the possibility of delaying the field penetration into the Nb layer, as predicted for SIS film structures.

The poorer entry field results for samples SIS-2, SIS-3 and SIS-4 are believed to be due to the lower surface quality of these films, as presented earlier. However, damage created at the thin film edges in the cutting process could also play some role, although the same procedure was followed and the same cut-off machine was used in preparation of all the investigated samples. In any case, the homogeneity and density of the surface layer is of utmost importance in order to provide the sought after shielding effect wanted from SIS films.

Figure 16 presents the DC magnetisation curves as a function of the applied field ($H_a$), measured at 4.2 K for the three component films of the SIS coatings: the single DC MS Nb layer, the single NbN layer used in the SIS films (Opt-1) and the best performing SIS film (SIS-1). In (a) the virgin magnetisation curves are presented, in a plot where the measured sample magnetic moment $m(H_a)$ is divided by a linear field dependence of the magnetic moment followed in the Meissner shielding state $m_{lin} = c H_a$ ($c$—constant, different value for each sample). Figure 16(b) displays the full magnetisation loops measured on the three samples. The deviation from the Meissner state, marked by the decline in $m/m_{lin}$, appears significantly earlier for the single NbN layer than the Nb and SIS films. The SIS film displays very similar curves to the Nb film. The magnetisation loops in (b) indicate the presence of the surface barrier to the magnetic flux penetration for both the SIS and Nb films, although there is no visible barrier in the single NbN film itself. The NbN layer instead presents a smooth curve, indicative of a stable flux pinning state.

4. Conclusion

The synthesis of high $T_c$ NbN has been achieved on polycrystalline Cu substrates with a maximum $T_c = 16.1$ K. The use of higher deposition pressures and lower $N_2$ flow rates leads to the formation of the higher $T_c \delta$-NbN (111) phase. The faceted nature of the film surface and the often disjointed columnar structure of these films results in a decrease in the entry field value, however. The application of a substrate bias provided improvements in the density of the high pressure films. On the other hand, films deposited at lower deposition pressures formed in the $\delta$-NbN (200) phase and displayed moderate $T_c \sim 12$ K with an increased entry field value up to a maximum of $H_{en} = 13.0$ mT at low $N_2$ flow rates. This is related to the denser film structure as well as the smoother
surface grain structure which characterises low pressure films. Overall, a lower $N_2$ content is recommended for superior NbN film synthesis on Cu.

Initial ML SIS films have been successfully deposited onto copper substrates. These films provide an indication of the possible enhancement of the entry field value associated with SIS films when compared to single layer Nb films. The performance of the SIS films is dependent on the homogeneity of the film surface and as such, is greatly affected by the roughness of the base Nb layer. Therefore, efforts should be made to first obtain a superior single layer Nb film on Cu, e.g. through the use of high power impulse magnetron sputtering, prior to focusing on SIS films themselves. Further study is also required to determine whether the moderate $T_c$, high entry field ($\delta$-NbN (200)) or the high $T_c$, low entry field ($\delta$-NbN (111)) films provide superior shielding for the base Nb layer in SIS film structures.

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