Superconducting properties of very high quality NbN thin films grown by high temperature chemical vapor deposition

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Abstract

Niobium nitride (NbN) is widely used in high-frequency superconducting electronics circuits because it has one of the highest superconducting transition temperatures ($T_c \sim 16.5$ K) and largest gap among conventional superconductors. In its thin-film form, the $T_c$ of NbN is very sensitive to growth conditions and it still remains a challenge to grow NbN thin films (below 50 nm) with high $T_c$. Here, we report on the superconducting properties of NbN thin films grown by high-temperature chemical vapor deposition (HTCVD). Transport measurements reveal significantly lower disorder than previously reported, characterized by an Ioffe–Regel parameter ($k_\parallel l$) $\sim 12$. Accordingly we observe $T_c \sim 17.06$ K (point of 50% of normal state resistance), the highest value reported so far for films of thickness 50 nm or less, indicating that HTCVD could be particularly useful for growing high quality NbN thin films.

Keywords: superconductivity, niobium nitride NbN, 2D material, Ioffe–Regel, strong coupling superconductor (Some figures may appear in colour only in the online journal)

1. Introduction

Niobium nitride (NbN) thin films—thanks to their high $T_c$ $\sim 16.5$ K, superconducting energy gap $\Delta \sim 2.5$ meV, and upper critical field $B_{c2} \sim 40$ T—have been the subject of intense research for the last few decades, both on application and fundamental grounds. The combination of high $T_c$ and small coherence length ($\xi(0) \sim 5$ nm) allows for ultra thin NbN films ($\leq 5$ nm) with reasonably high $T_c$, which is essential for, e.g., superconducting single photon detectors (see e.g. [1, 2]) as well as hot electron bolometers. NbN has higher kinetic inductance than most other S-wave superconductors [3], which helps fabricating superconducting microwave resonators with high characteristic impedance and microwave kinetic inductance detectors. On the fundamental level, the effects of disorder on superconducting and normal state properties have been studied in NbN thin films [4–6].

Nano-wires, made from NbN thin films, have demonstrated thermal and quantum phase slips [7]—a phenomenon of great interest in understanding one-dimensional superconductivity. Further, the large superconducting energy gap of NbN can be explored in designing circuit quantum electrodynamics experiments in the THz frequency range.

Thus, there has been a growing demand of high quality NbN thin films. Reactive DC magnetron sputtering from an Nb target in an argon and nitrogen atmosphere is most commonly used to deposit NbN on various substrates [8–11]. In this process, films with $T_c \sim 16.0$ K have been routinely produced; however, for films with thickness $\sim 5$ nm, the $T_c$ decreases significantly. The main difficulty in this process arises from the creation of atomic level nitrogen vacancies and from the formation of non-superconducting Nb$_2$N and...
hexagonal phases. Besides, in the optimal parameter range, the high sputtering rate (typically $\sim 1$–5 nm s$^{-1}$) makes it difficult to control the thickness below 10 nm. Some other methods, where the superconducting properties of NbN thin films were probed, include pulsed laser deposition [12–14], molecular beam epitaxy [15] and atomic layer deposition [16]. In this regard, deposition of superconducting NbN films by high temperature chemical vapor deposition (HTCVD) is rather rare. HTCVD, compared to most of the other methods, has certain advantages: it is cost effective, especially for large scale productions and the growth rate being tunable to low values (down to 1 mm min$^{-1}$), it is easy to control the thickness of the films.

As a first step to explore HTCVD as an alternative to the existing methods to produce good quality superconducting NbN films, we grow three 49 nm thick NbN films by HTCVD, and investigate their superconducting properties. The free electron density ($n$) of the films is determined from Hall measurements at room temperature. The zero temperature upper critical field $B_{c2}(0)$ and the Ginzburg–Landau coherence length $\xi(0)$ are estimated from magnetoresistance data near $T_c$. The strong coupling nature of our NbN films is confirmed by superconducting energy gap (\Delta) measurement of a film by scanning tunnel spectroscopy (STS) at 1.35 K. We also estimate $\lambda(0)$ from the normal state resistivity ($\rho_{xx}$) and $\Delta(0)$. Our best film has very high $k_F\ell \sim 12$ and $T_c \sim 17.06$ K, and quite low $\rho_{xx} \sim 70 \mu\Omega cm$ and $\lambda(0) \sim 185$ nm, making it very promising for many superconducting applications.

2. Experiments and results

Three 49 nm thick NbN films, labeled S2, S3, and S4 were grown simultaneously (under the same process condition) at 1300 °C on different sapphire substrates by HTCVD. These are the exact films whose deposition process, thickness determination, and the structural characterizations have already been reported elsewhere [17]. Briefly, S2 and S4 were grown on (1120) and (0001) oriented sapphire ($Al_2O_3$) substrate, respectively; whereas, S3 was grown on (0001) oriented $Al_2O_3$ with a buffer layer of 80 nm thick aluminum nitride (AlN) grown by HTCVD [18]. X-ray diffraction and high resolution transmission electron microscopy (HRTEM) studies reveal that all the NbN-films contain face centered cubic (FCC) as primary phase, grown preferentially along the (111) orientation. The average out-of-plane lattice parameters ($a$) are listed in table 1. Apart from the (111) preferential orientation, all the films also show additional orientations (mainly 200). The $f$ factors—a measure of the degree of preferential orientation for FCC films [19]—are also listed in table 1. S2 only contains cubic phases, whereas S3 and S4 also contain a very small fraction of hexagonal phases, more in S3 than in S4.

The thicknesses of the films were first measured using an x-ray reflectivity technique in a PANalytical X’pert Pro MPD diffractometer. Subsequently, the thickness values were confirmed by direct HRTEM measurement on sample S3 and S4 [17].

The electrical transport measurements were performed down to 4 K in a commercial Physical Property Measurement System. In figure 1, we plot the temperature variation of resistivity ($\rho_{xx}$) for S2, S3, and S4. The normal state resistivities $\rho_{xx}$ of the films, defined at $T = 17.25$ K, are listed in table 1. In the normal state, the resistivity has very little variation in temperature as evident from residual resistivity ratio, defined as $\rho_{xx}(270.0$ K)/$\rho_{xx}(17.25$ K), listed in table 1. The inset of figure 1 shows the superconducting transition of resistivity on a log scale. The $T_c$ of the films, defined as the temperatures where resistivity is half of the normal value, are listed in table 1.

In figure 2, we plot the Hall resistivity ($\rho_{xy}$) for all three samples. The electron density ($n$) was estimated from the slope, known as the Hall resistance $R_H = 1/ne$, where $e$ is the charge of an electron. The Hall measurement was performed at room temperature where electron–electron interaction is expected to be weak [20], justifying the free electron approximation. $R_H$ values at room temperature for all three samples are listed in table 1. Knowing $n$ and $\rho_{xx}$, the elastic scattering time ($\tau$) was estimated from Drude’s formula: $\rho_{xx} = m/ne^2\tau$, here, $m$ is the mass of a free electron. The other important parameters—the Fermi wave vector ($k_F$), the Fermi velocity ($v_F$), the mean free path ($\ell$), and the diffusion constant ($D$)—were estimated from the following formulas: $k_F = (3\pi^2n)^{1/3}$, $v_F = hk_F/m$, $\ell = v_F\tau$, $D = v_F\ell/3$. In table 2, we summarize these parameters together with $k_F\ell$.

In figure 3, we present the magneto-resistance data for S3. Figure 3(a) presents the variation of $\rho_{xx}$ as a function of temperature for magnetic fields from 0 to 8 T. The graph clearly shows that the zero temperature value of the upper critical field ($B_{c2}(0)$) is greater than 8 T, the maximum field our setup could provide. We, therefore, extract $B_{c2}(0)$
Table 1. Summary of the experimental results. Here, $\rho_{sx}$ is the normal state resistivity at 17.25 K. $T_c$ is defined at a temperature where resistivity is half of $\rho_{nx}$. The residual resistance ratio (RRR) is taken as the ratio of $\rho_{nx}$ between 270 and 17.25 K.

| Samples | Substrate      | $a$  | $f$ factor | $R_H$ ($10^{-3} \mu\Omega \cdot cm$ T$^{-1}$) | $\rho_{sx}$ ($\mu\Omega \cdot cm$) | RRR  | $T_c$ (K) | $\Delta T_c$ (K) | $\frac{d\rho_c}{dT}$ at $T_c$ (T K$^{-1}$) |
|---------|----------------|------|------------|---------------------------------------------|------------------------------------|------|-----------|------------------|-------------------------------------------|
| S2      | Al$_2$O$_3$ (1120) | 4.436 | 0.92       | 5.6                                         | 70.0                               | 1.05 | 16.80     | 0.55             | 0.96                                       |
| S3      | AlN (0001)      | 4.344 | 0.99       | 6.9                                         | 76.6                               | 1.11 | 17.02     | 0.32             | 0.99                                       |
| S4      | Al$_2$O$_3$ (0001) | 4.427 | 0.98       | 5.0                                         | 62.8                               | 1.0  | 17.06     | 0.32             | 0.96                                       |

Figure 2. The Hall resistivity for all three samples at room temperature. The magnetic field was scanned from 0 to 8 T. The electron densities, listed in Table 1, are estimated from the slope ($R_H$) using the formula: $R_H = 1/ne$.

from the following formula: $B_{c2}(0) = 0.69T_c \left| \frac{d\rho_c}{dT} \right|_{T_c}$ [21]. The slope near $T_c$, $\left( \frac{d\rho_c}{dT} \right)_{T}$, was extracted as shown in Figure 3(b). Here, we plot the variation of resistance as a function of magnetic field at different temperatures near $T_c$. The inset shows the variation of $B_{c2}$, defined as the field where the resistivity is half the normal state value of $\rho_{sx}$ (taken at 17.25 K), as a function of temperature. The slope is extracted from the straight line fit, indicated by the solid line. We also extract $\xi(0)$ from the slope, using the following formula: $\xi(0) = \sqrt{\Phi_0/2\pi T_c \left( \frac{d\rho_c}{dT} \right)_{T_c}}$ [22]. In Table 2, we summarize both $B_{c2}(0)$ and $\xi(0)$.

In order to estimate the zero temperature superconducting energy gap $\Delta(0)$ of our films, we have performed STS measurements on S2 at $T = 1.35$ K, a temperature much lower than $T_c$. $\Delta(0)$ is found to be inhomogeneous over space—it’s value ranging from 2 to 2.8 meV. The spatial variation of the gap seemed to be correlated with the grain morphology with typical size scale of about 100 nm, the smaller gap being located in the middle of the grains and the larger gaps on their edges. However, we also observed locally strongly suppressed superconducting gaps which might also be due to local contamination or oxidation of the surface as the sample had been exposed to air over a period of more than one year prior to STS measurements. Figure 4 shows an experimental spectrum and a fit computed with a gap of 2.8 meV according to Bardeen–Cooper–Schrieffer theory [23]. This leads to a ratio $2\Delta/k_B T_c = 4$, which is slightly less than values reported in literature [6, 10].

3. Discussion

We have, so far, extensively used free electron model (FEM) to estimate various parameters like $n$ or $k_F \ell$. The FEM, in general, works very well for good metals. On the other hand, unlike a good metal, our films have very little variation in resistivity as a function of temperature in the normal state (Figure 1). Thus, it is not obvious that the FEM should work well. In this regard, we observe that the free electron densities $n$ of our films are significantly lower than the theoretical estimate of $n = 2.39 \times 10^{20} \text{ m}^{-3}$ [24]. The other important parameter to compare, as suggested by Chockalingam et al. [10], is the density of states (DOS) at the Fermi level. The DOS per unit volume, in the framework of FEM, is given by: $N_F = nk_F/k_B^2n^2$. The DOS per NbN unit, $N_n$, listed in Table 1, is then $N_n = N_F a^3/4$ (each unit cell of volume $a^3$ is shared by 4 NbN units). Contrary to the electron density $n$, we see that the estimated DOSs are quite close to the theoretical estimate of 0.54 eV$^{-1}$ [25] or from the specific heat measurement $\approx 0.5$ eV$^{-1}$ [26].

The critical temperature $T_c \sim 17$ K of our films is, to the best of our knowledge, the highest reported to date for NbN thin films with thickness 50 nm or less. The $T_c$ values stated in Table 1 are defined as the point of 50% of the normal state resistance (taken at 17.25 K). The resistivity reaches 1% of the normal state resistance at 16.60 K, 16.89 K, and 16.91 K for S2, S3, S4, respectively. These numbers are still significantly higher than previously reported numbers and show that the superconducting transition is very sharp. This, we believe, is the result of the epitaxial nature and good crystallinity of our films, that lead to $k_F \ell$ values significantly higher than the ones reported previously (see e.g., [5, 10]). The increase in $k_F \ell$ reduces the electron–electron Coulomb repulsion [27], which according to McMillan’s theory [28] enhances the $T_c$. The other possible reason behind the high value of $T_c$ could be the large tensile strain which is known to enhance $T_c$ in epitaxial thin films. In fact, in our previous study [17], we calculated that our films exhibit a large tensile stress up to 5 GPa, much larger than the films grown by sputtering [29].

The presence of carbon impurities, as was observed by William et al. [30], can also enhance $T_c$. However, chemical...
analysis using an Electron Probe Micro Analyzer showed that the carbon content in the films is less than the detection limit of this technique (less than 5%) [17].

Chand et al [5] reported \( T_c \sim 17.0 \) K for one of their sputtered NbN films with thickness over 50 nm. For sputtered NbN films, the enhancement of \( T_c \) with thickness has been observed even above 100 nm [9]. Chockalingam et al [10] also observed a systematic increase in \( T_c \) with \( n \) or DOS at the Fermi level. We do not observe such trend. Wang et al [9] observed a systematic non-monotonic variation of \( T_c \) with \( n \); the highest \( T_c \), they observed, was for \( n = 4.46 \) Å.

The upper critical field \( B_{c2} \) is very similar for all of our films, but much lower than for films with \( T_c \) higher than 14 K reported in the literature [10, 31, 32]. In the dirty limit, defined by \( \ell \ll \xi(0) \) for our films, a further indication that our films have lower disorder, i.e. larger diffusion constant/ lower resistivity. Indeed, the resistivities \( \rho_{xx} \sim 70 \mu \Omega \text{cm} \) we observe are significantly lower than previously reported [10, 31, 32]. One should note, however, that the above formula yields \( B_{c2}(0) \approx 3.0 \) T for our films, significantly lower field than the value extracted from figure 3. This discrepancy could be due to the spin–orbit interaction, which has not been taken into account in the above formula and can enhance \( B_{c2}(0) \) very significantly [34].

Next we estimate the zero temperature value of the magnetic penetration depth \( \lambda(0) \) from \( T_c \), using the following formula [35]: \( \lambda^2(0) = \pi \mu_0 \Delta(0)/h \rho_{xx} \). For NbN films, this formula is found to closely match experiment [35]. The calculated \( \lambda(0) \) are listed in table 2. In our calculation, \( \Delta(0) \) is estimated from strong coupling relation \( 2\Delta(0)/k_B T_c = \pi \) assuming \( \alpha = 4.00 \) for all three films. S4, as we see from table 2, has minimum \( \lambda(0) \) among the three films, which is due to its highest \( T_c \) and lowest \( \rho_{xx} \) values.

![Figure 3](image1.png)

**Figure 3.** (a) The variation of resistivity \( \rho_{xx} \) of S3 as a function of temperature for magnetic fields 0 to 8 T. (b) The variation of \( \rho_{xx} \) as a function of magnetic field at different temperatures, 16.2–16.7 K with increments of 0.1 K, near \( T_c \). The inset shows the variation of \( B_{c2} \) as a function of temperature, with \( B_{c2} \) being defined as the field where the resistance is half of the normal state resistance at 17.25 K. The straight line fit, indicated by the solid line, gives the slope used to determine \( B_{c2}(0) \) and \( \xi(0) \), listed in table 2.

![Figure 4](image2.png)

**Figure 4.** Normalized tunneling conductance versus bias voltage at 1.35 K on sample S2 (black points). The red curve is a BCS theoretical fit with a superconducting gap of 2.8 meV.

![Table 2](table2.png)

**Table 2.** Summary of the various parameters calculated from the experimental results of table 1.

| Samples | \( n \) \((10^{29} \text{ m}^{-3})\) | \( \tau \) \((\text{fs})\) | \( \ell \) \((\text{nm})\) | \( D \) \((\text{cm}^2 \text{ s}^{-1})\) | \( k_B \ell \) | \( \mu_0 N(\ell)\) \((\text{eV})^{-1}\) | \( B_{c2}(0) \) \((\text{T})\) | \( \xi(0) \) \((\text{nm})\) | \( \lambda(0) \) \((\text{nm})\) |
|---------|----------------|--------|---------|----------------|----------|----------------|----------------|---------|---------|
| S2      | 1.1            | 0.46   | 0.79    | 4.5            | 11.4     | 0.43           | 11.1           | 6.5     | 192     |
| S3      | 0.9            | 0.52   | 0.83    | 4.5            | 11.4     | 0.40           | 11.3           | 6.5     | 199     |
| S4      | 1.22           | 0.46   | 0.81    | 4.8            | 12.3     | 0.45           | 11.7           | 6.4     | 181     |
Finally, we estimate the errors in the important parameters of our samples. Two main sources of errors, in the quantities we have calculated, are the uncertainty in the thickness measurement and shape asymmetry (imperfection in the Hall geometry), which are about 10% and 5%, respectively. These propagate error to $\rho_{xx}$, $n$, $k_0 \ell$ and $\lambda(0)$ about 15%, 10%, 12%, and 13%, respectively. The temperature, on the other hand, could be measured within 50 mK accuracy.

4. Summary

In summary, we have found exceptionally high critical temperatures around 17 K and large superconducting gap of 2.8 meV for NbN films grown by HTCVD at 1300 °C on sapphire and AlN. We explain this high critical temperature by very large $k_0 \ell$ parameters indicating low disorder. In agreement with this interpretation, we observe low resistivity ($\sim 70 \mu \Omega \mathrm{cm}$) and low upper critical field ($\sim 11$ T). Our results demonstrate that HTCVD, a particularly cost effective growth technique, is a very promising alternative to magnetron sputtering for depositing high-quality NbN thin films. A natural extension of this work will be to further investigate the existing links between the material characteristics and the superconducting properties and to explore the limits of the HTCVD techniques for the production of high quality ultra thin films of NbN.

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