Molecular Beam Epitaxy of Transition Metal Nitrides for Superconducting Device Applications

D. Scott Katzer,* Neeraj Nepal, Matthew T. Hardy, Brian P. Downey, David F. Storm, Eric N. Jin, Rusen Yan, Guru Khalsa, John Wright, Andrew C. Lang, Tyler A. Growden, Vikrant Gokhale, Virginia D. Wheeler, Alan R. Kramer, Joan E. Yater, Huili Grace Xing, Debdeep Jena, and David J. Meyer

Epitaxial integration of superconductors with semiconductors is expected to enable new device architectures and to increase electronic circuit and system functionality and performance in diverse fields, including sensing and quantum computing. Herein, radiofrequency plasma molecular-beam epitaxy is used to epitaxially grow 3–200 nm-thick metallic NbNx and TaNx thin films on hexagonal SiC substrates. Single-phase cubic δ-NbN and hexagonal TaNx films are obtained when the starting substrate temperature is ≈800 and ≈900 °C, respectively, and the active N to Nb or Ta ratio is ≈2.5–3. The films are characterized using in-situ reflection high-energy electron diffraction and ex-situ atomic force microscopy, contactless sheet resistance, X-ray diffraction, X-ray photoelectron spectroscopy, secondary ion-mass spectrometry, Rutherford backscattering spectrometry, cross-sectional transmission electron microscopy, and low-temperature electrical measurements. Smooth, epitaxial, low-resistivity films of cubic δ-NbN and hexagonal TaNx on SiC are demonstrated for films at least ≈50 nm-thick, and their superconducting properties are reported. Epitaxy of AlN and GaN on δ-NbN is also demonstrated, as well as integration of an epitaxial NbNx superconducting electrode layer under GaN high-electron mobility transistors. These early demonstrations show the promise of direct epitaxial integration of superconducting transition metal nitrides with group III-N semiconductors.

1. Introduction

Although the advantages of epitaxial metal layers in devices such as metal-base transistors, including low base resistance and small base transit time, were predicted as early as the 1960s,[1] the successful realization of high-quality epitaxial metals on semiconductors, and semiconductors on metals, has remained elusive. Sands et al. reviewed the progress and status of research on epitaxial metals on III–V compounds in 1990.[2] More recently, researchers have investigated ZrB2[3–5] and TiC[6,7] metallic substrates for GaN heteroepitaxial growth and device fabrication, and superconducting cubic niobium nitride (NbNx) has been grown on GaN and AlGaN by sputtering.[8,9] NbNx and tantalum nitride (TaNx) are transition metal nitrides (TMNs) (also called “interstitial nitrides”) with many compelling properties.[10] TMNs such as NbNx have been studied for decades and have many practical applications due to their mechanical, chemical, and electrical properties.[11] The cubic δ-NbN crystalline phase of NbNx is a well-known superconductor which has been used for superconducting...

Less well-known, hexagonal β-Nb2N is another one of the several stable phases of niobium–nitrogen compounds that is of particular interest for epitaxial growth. Hexagonal β-Nb2N and the corresponding hexagonal phase γ-Ta2N are members of the P63/mmc space group, with the lattice parameters a = 0.3056 nm and c = 0.30476 nm for Nb2N and a = 0.30476 nm and c = 0.49187 nm for Ta2N.[17] As shown in the VESTA ball-and-stick crystal models in Figure 1a,b,[18] these hexagonal phases have a near-lattice-matched hexagonal structure that is similar but not identical to the hexagonal structure of 6H-SiC (P63/mmc, a = 0.3081 nm, c = 1.510 nm).[19] Hexagonal SiC substrates are technologically important for the heteroepitaxial growth of high-performance III–N materials due to their high thermal conductivity. Figure 1c shows that the [111]-oriented cubic δ-NbN crystalline phase with space group Fm3m and a = 0.446 nm (pseudo-hexagonal a = 0.446 nm /√2 = 0.315 nm) also has close atomic registry to SiC. There is still some controversy about the crystalline phases of TaN compounds, with the hexagonal δ-TaN phase having been variously identified as the WC-like phase (P6m2), P63/mmc,[17] and wurtzite (P63/mc).[19] Note that the N-site occupancy is ideally 0.5 for the Nb2N and Ta2N hexagonal phases, whereas it is ideally 1.0 for the cubic NbN phase and the hexagonal TaN phase. Other TMNs that could be considered for epitaxial integration with SiC and III-N semiconductors include TiN, ZrN, HfN, VN, MoN, and WN.[21]

The wide bandgap group III nitride semiconductors are also members of the P63/mmc space group like SiC. They have shown promise in a variety of modern electronics systems including ultrafast microwave communications,[22] ultralow-power computation,[23] high-voltage switches,[24] infrared through visible- to ultrafast microwave communications,[22] ultralow-power computation,[23] high-voltage switches,[24] and high-frequency circuit components such as surface acoustic wave and bulk acoustic wave filters.[25] Substantial advances in electronic systems would be expected if the electronic functionality of group III-N semiconductors could be combined with that of superconductors on a single epitaxial platform.[26–31] Integration of 2D superconducting gallium layers has been reported recently on GaN and other substrates.[32–34]

Little has been reported on the epitaxy of hexagonal phases of TMNs on hexagonal substrates for integration with III-N semiconductor devices to date. The promise of achieving a near-lattice-matched hexagonal metal to hexagonal III–N materials by changing only the cation from Ga or Al to Nb or Ta makes Nb2N and Ta2N, and hexagonal TaN, especially intriguing for use in III–N epitaxy compared with TiC[3–5] or ZrB2[6,7] where both the cation and anion change across the interface. There has also been little reported on the superconducting properties of the hexagonal phases, other than they are known to either not be superconducting or to have much lower transition temperatures than the cubic phase.

Here, we review progress in the epitaxial growth of NbN, and TaN on SiC using molecular beam epitaxy (MBE), discuss the properties of the materials, and demonstrate successful epitaxial integration of the superconducting III-N and superconducting TMN materials families as a crucial enabler for future superconducting device applications.

### 2. MBE of TMNs on SiC

In this section, the system used for the MBE growth of TMNs on hexagonal 4H- and 6H-SiC substrates is discussed along with its important features. The use of equilibrium phase diagrams to understand and reduce the growth space investigated, and thereby more rapidly climb the growth learning curve, is also described. Finally, the growth conditions used to grow NbN, and TaN TMNs epitaxially on SiC are described.

![Figure 1. Ball-and-stick crystal models of the epitaxial TMNs on SiC considered here. a) hexagonal β-Nb2N, b) hexagonal γ-Ta2N, c) [111]-oriented cubic δ-NbN, and d) hexagonal (wurtzite) δ-TaN. Note that the ideal N-site occupancy is 0.5 for the hexagonal Nb2N and Ta2N phases and 1.0 for the cubic NbN, and the hexagonal TaN phases.](image-url)
2.1. MBE Growth System

The epitaxial growth was performed in a customized Scienta-Omicon PRO-75 MBE growth chamber with liquid-nitrogen cooled cryopanels having a base pressure below \( 2 \times 10^{-11} \) Torr, as described previously\(^{[35,36]} \). Niobium and tantalum have extremely low vapor pressures below the 2000 °C temperature limit of conventional effusion cells, so electron beam (e-beam) evaporation is the only practical method to evaporate these elements in a UHV system. The niobium flux, \( f_{\text{Nb}} \), and tantalum flux, \( f_{\text{Ta}} \), were generated by an in-situ 5 kW e-beam evaporator. The elemental niobium or tantalum source material was 99.95% pure Nb (excluding Ta at 90 ppmw) or Ta pellets (Nb at 26 ppmw), with the principal impurities being O, C, W, and N loaded in a W hearth liner. The incident reactive nitrogen flux, \( f_{\text{N}_2} \), was generated by a Veeco Uni-Bulb RF-plasma source using a 99.9999% pure \( \text{N}_2 \) gas that was further purified using an inline purifier. The flux from a Uni-Bulb RF-plasma source is typically found to be a mixture of atoms, ions, and excited molecules\(^{[37]} \) but was not characterized further in this study.

Reflection high-energy electron diffraction (RHEED) was performed in-situ in the PRO-75 using a Staib Instruments RH20 RHEED system operated at 13.5 keV accelerating voltage and 1–2 μA beam current. The e-beam evaporator electromagnets caused a \( \approx 1 \) cm lateral shift in the RHEED pattern when the e-beam was at high voltage, but they did not otherwise significantly disturb the RHEED images.

2.2. MBE Growth Conditions for TMNs and Heterostructures

Figure 2 shows the equilibrium phase diagrams for a) Nb–N compounds and b) Ta–N compounds\(^{[38]} \). Although MBE is in general not an equilibrium growth process, the phase diagrams can allow us to make inferences about the expected growth conditions necessary to obtain single-phase materials and to be aware of potential complications. For example, the Nb–N phase diagram indicates that at atmospheric pressure a minimum temperature of around 780 °C is needed for the formation of the hexagonal \( \beta\)-Nb–N phase, whereas temperatures above 1200 °C are needed to form the so-called “high-temperature” phase cubic \( \delta\)-NbN\(_x\). Another important detail to note is that the \( \beta\)-Nb–N and \( \delta\)-NbN\(_x\) crystalline phases exist over a fairly wide composition range, and in fact both crystalline phases can exist in certain composition ranges (N-rich \( \beta\)-Nb–N and N-lean \( \delta\)-NbN\(_x\)). For the case of Ta–N, the shape of the phase diagram is similar, but the hexagonal \( \delta\)-TaN\(_x\) phase is well separated on the composition axis from the hexagonal \( \gamma\)-TaN\(_x\) phase. Therefore, we might expect that the hexagonal Ta–N or TaN phase purity would be easier to control compared with the niobium case. Since these equilibrium phase diagrams are very similar (except that higher minimum temperatures are generally required for TaN\(_x\) phase formation), one could expect to be able to transfer NbN\(_x\) MBE growth knowledge to epitaxial TaN\(_x\) by using similar flux conditions and simply increasing the TaN\(_x\) growth temperature above that used for NbN\(_x\). We investigated the growth parameter space of NbN\(_x\) and found this to be the case. In particular, the MBE growth window for single-phase TaN\(_x\) seems to require substrate temperatures greater than \( \approx 900 \) °C to obtain single-phase epitaxial material on SiC when using N-rich MBE growth conditions, whereas temperatures above \( \approx 775 \) °C are required for single-phase NbN\(_x\), as discussed below\(^{[39,40]} \).

Since the stable NbN\(_x\) and TaN\(_x\) films exist over a range of compositions and exhibit multiple crystal structures, the niobium-based TMN films will be referred to hereafter as “NbN\(_x\)” and the tantalum-based TMN films will be referred to as “TaN\(_x\)” unless we are specifically addressing their crystalline phase. We will also use “TMN” below to refer to either NbN\(_x\) or TaN\(_x\) (but not other TMN compounds).

TMN thin films were grown on 3-in.-diameter [0001]-oriented semi-insulating (Si) Si-face 6H- or 4H-SiC substrates that had been chemically–mechanically polished to an epi-ready finish. No ex-situ cleaning or backside metallization of the substrates was performed in this study. After the SiC substrate was thermally cleaned in the MBE growth chamber at temperatures of

![Figure 2](image-url)

**Figure 2.** Equilibrium phase diagram for a) niobium and nitrogen, and b) tantalum and nitrogen. Note that both TMN systems are quite complex, but they are qualitatively similar for the hexagonal phases of interest except for the higher temperatures required for phase formation in the tantalum-nitrogen case. The hexagonal \( \beta\)-Nb–N, cubic \( \delta\)-NbN\(_x\), hexagonal \( \gamma\)-TaN\(_x\), and hexagonal \( \delta\)-TaN\(_x\) phases of interest are highlighted. Reproduced with permission\(^{[40]} \). Copyright 2019, American Institute of Physics.
≈800–900 °C for 10 min, the substrate temperature was changed to the desired fixed value and allowed to stabilize. To date, in experiments using nitrogen-rich growth conditions, the substrate temperature is the most important growth parameter controlling the TMN metallic film growth on SiC. It should be noted that the real temperature of radiatively heated substrates can increase dramatically as a result of increased IR absorption during the MBE growth of semiconductors with bandgaps smaller than the substrate.[43] The deposition of zero-bandgap metals on a wide-bandgap substrate would also lead to more reflection of IR radiation back toward the substrate heater thermocouple as the thickness increased. Thus, the evolution of the TMN/SiC surface temperature may be expected to be a strong function of the TMN thickness and deposition conditions. For simplicity, all of the growth temperatures discussed here were the starting temperatures of the SiC substrate, estimated by scaling the substrate heater thermocouple temperature which was calibrated via excess Ga surface coverage measurements during GaN growth.[42]

While the substrate temperature was stabilizing, the e-beam source was set to operating conditions to achieve the desired fNb or fTa, and the N+ plasma was started. The TMN deposition rate was principally determined by the fNb or fTa and was typically 1.2 nm min⁻¹ (≈1.1 × 10⁻¹⁴ cm⁻² s⁻¹), as measured using a quartz crystal microbalance (QCM). The RF-plasma power levels were ≈25 W higher than the minimum required for a stable “high-brightness” plasma (i.e., 250–370 W depending on the age of the source’s plasma chamber), and the N₂ flow rate was in the range of 0.8–1.2 sccm. The chamber pressure during growth was 1–2 × 10⁻⁵ Torr. The resultant fN* was nominally ≈3.3 nm min⁻¹ as determined from measured N-limited GaN growth rates. Note that the implicit simplifying assumption that fN* incorporates in TMN the same way as it does in GaN is unlikely to hold because TMNs can form without excited nitrogen. However, relating the fN* to an equivalent N-limited GaN growth rate is a helpful metric for comparison to conventional III-N MBE growth conditions. After a 10 min plasma stabilization delay, the TMN growth was initiated by opening the N⁺, e-beam, and substrate shutters sequentially, and the growth continued until the desired thickness was reached.

In samples where III-N heterostructures were grown in situ immediately after the TMN growth was completed, the e-beam evaporator was returned to a low-power state, the substrate temperature and N⁺ fluxes were adjusted to the values needed for III-N epitaxy, and the III-N growth was then started in the usual way as if the growth were being performed directly on SiC.

### 3. Characterization of TMNs and III-N/TMN Heterostructures

In this section, the various characterization methods used to determine the properties of the TMN films are described along with the results obtained. Section 3.1 discusses in-situ RHEED. Section 3.2 is the first of several sections on ex-situ measurements and includes atomic force microscopy (AFM). Section 3.3 describes contactless sheet resistance measurements and results. Section 3.4 gives an overview of X-ray diffraction (XRD) measurements. Selected samples were characterized by methods discussed in Section 3.5 to directly extract chemical composition information—X-ray photoelectron spectroscopy (XPS), Rutherford backscattering spectrometry (RBS), and secondary ion mass spectroscopy (SIMS). Section 3.6 discusses transmission electron microscopy (TEM) results obtained on selected samples. Finally, Section 3.7 presents electronic and superconducting properties of several MBE-grown TMN structures.

#### 3.1. Reflection High-Energy Electron Diffraction (RHEED)

When the MBE growth conditions for the TMN films are correctly optimized, the RHEED pattern changes smoothly at the initiation of film growth without the appearance of island-induced roughness on the Si-face hexagonal SiC substrate. Moreover, the streaky RHEED pattern is maintained throughout the remainder of the TMN film growth. Figure 3a shows the post-growth RHEED pattern observed on a 20-nm-thick NbNₓ film grown on 6H-SiC. A clear, bright, 2 × 2 reconstruction was present on this surface. Figure 3b shows the post-growth RHEED pattern observed on a 43-nm-thick TaNₓ film grown on 6H-SiC. A clear, bright, 3 × 1 reconstruction was present on this surface. Wang et al. reports that a 2 × 2 reconstruction is a signature of N-lean NbNₓ epitaxy[43] whereas Figure 3b is the first known report of a surface reconstruction on TaNₓ. All of the high-quality NbNₓ and TaNₓ films grown on hexagonal SiC by MBE have had a sixfold in-plane rotational symmetry in RHEED. Smoother TMN films generally correlated with smooth, streaky RHEED patterns.

As in other material systems, RHEED can be used for optimizing the growth conditions (especially the growth temperature) of the TMN films grown on SiC. In general, spottiness in the RHEED pattern, especially in the first 5–10 nm of growth, is usually an indication that the substrate temperature is too low. In contrast, rapid dimming of the RHEED pattern can be an indication that the epitaxy is degrading and the surface is rapidly roughening, which may indicate that excessive nitrogen is being lost from the film because the substrate temperature is too high for the fN* used.

#### 3.2. Atomic Force Microscopy (AFM)

TMN samples were characterized by AFM using a Bruker Fast Scan system operated in tapping mode. Figure 4a shows a 1 × 1 μm² AFM image of the surface of a 20-nm-thick NbNₓ epitaxial film having a root mean square (rms) roughness of 0.46 nm.[39] The rms roughness often increases with NbNₓ thickness, but the surface is still smooth (i.e., rms < 0.5 nm) for films at least 200 nm thick if the growth conditions are optimized. For very thin films with thicknesses below 10 nm, the surface roughness is basically unchanged from the roughness of the epi-ready SiC substrate (rms roughness as low as ≈0.1 nm), and the NbNₓ film retains the atomic step morphology of the underlying SiC.

Figure 4b shows representative post-growth 10 × 10 μm², 3 × 3 μm², and 1 × 1 μm² AFM scans of the same 43-nm-thick TaNₓ film shown in Figure 3b.[40] The film is smooth over all three length scales with rms roughnesses less than 0.5 nm in each case (as indicated by the numbers inset in the images). The 3 × 3 μm² scan shows faint, nearly parallel lines that are surface steps mimicking those in the starting SiC surface.
Figure 3. a) Post-growth RHEED patterns for 20-nm-thick NbN film grown on 6H-SiC. Note the clear, bright, \(2 \times 2\) reconstruction. Reproduced with permission.[39] Copyright 2015, IOP Publishing. b) Post-growth RHEED pattern for 43-nm-thick TaN film grown on 6H-SiC. Note the clear, bright, \(1 \times 3\) reconstruction. Reproduced with permission.[40] Copyright 2019, American Institute of Physics.

Figure 4. a) Post-growth AFM image for 20-nm-thick NbN film grown on 6H-SiC. The rms roughness is 0.46 nm. Note that the film reproduces the step-edges of the starting SiC substrate. Reproduced with permission.[39] Copyright 2015, IOP Publishing. b) Post-growth AFM images for 43-nm-thick TaN film grown on 6H-SiC. The film is very smooth, having rms roughness <0.5 nm for all scan ranges between 10 \(\times\) 10 \(\mu\)m\(^2\) and 1 \(\times\) 1 \(\mu\)m\(^2\). Reproduced with permission.[40] Copyright 2019, American Institute of Physics.
The $1 \times 1 \mu \text{m}^2$ image shows a fine surface grain structure without any obvious orientation dependence. No attempt was made to deconvolute the tip geometry in the $1 \times 1 \mu \text{m}^2$ scan. In general, smooth epitaxial TMN films can be grown by MBE on SiC and the surface morphology is similar for NbN$_x$ and TaN$_x$ films.

3.3. Contactless Sheet Resistance Measurements

Contactless sheet resistance measurements of the TMN films were performed with a Lehighton Electronics 1510B system. Figure 5a shows a summary of room temperature contactless resistivity measurements of several NbN$_x$ and TaN$_x$ films grown at 800 and 900°C, respectively, with differing thicknesses. The sheet resistance measurements were taken on a 55-point grid covering the 3-in.-diameter substrate (with 0.1-in. edge exclusion). The resistivity values shown in Figure 5a are the minimum measured values. Excellent resistivity uniformity was obtained on many samples: for example, a 40-nm-thick NbN$_x$ sample had a uniformity value (defined as standard deviation divided by the mean) of 2.2%. The minimum NbN$_x$ resistivity measured was 40 μΩ cm for a 100-nm-thick sample grown at 800°C. This is substantially lower than the ≈80–90 μΩ cm resistivity reported for 1-μm-thick sputtered NbN$_x$ films on Si substrates. As the thickness decreases from 100 to 30 nm, the film resistivity remains approximately constant at 40 μΩ cm. For thicknesses below 30 nm, the resistivity increases rapidly as the film thickness decreases, likely due to increased carrier scattering by the interfaces.

The minimum resistivity of a 43-nm-thick TaN$_x$ sample was 66 μΩ cm. As expected, the resistivity trend with TaN$_x$ thickness is similar to the case for NbN$_x$, with the points shifted up due to the higher resistivity of tantalum compared with niobium. However, to date, the resistivity of very thin TaN$_x$ films is substantially higher than that of comparable-thickness NbN$_x$ films.

These measurements have not been corrected to account for the formation of few-nm-thick NbO$_x$ and TaO$_x$ native surface oxides, which may be important when characterizing the resistivity of very thin air-exposed films. The thickest TaN$_x$ film resistivity is higher than the trend value, likely due to the need for more growth optimization for very thick films.

Figure 5b shows the contactless sheet resistance measured at 55 points across the 3-in.-diameter 43-nm-thick TaN$_x$/6H-SiC sample grown at 900°C. The lowest sheet resistance is in the center, as is typical for most MBE-grown TMN films. The sheet resistance nonuniformity across the wafer is 28.8%. The relatively high nonuniformity is expected to be reduced with further optimization of the TMN MBE growth process.

3.4. X-ray Diffraction (XRD)

XRD measurements were performed using a 9 kW Rigaku SmartLab system equipped with a rotating copper anode. Figure 6 shows a summary of the XRD results for 100-nm-thick NbN$_x$ films grown by MBE on SiC at several fixed substrate temperatures for similar Nb and N$_x$ fluxes. Measurements from the sample grown at 675°C show weak diffraction peaks at angles corresponding to the reported peak positions for: the metastable hexagonal δ phase with $x \approx 0.97$, the ε phase with $x \approx 1.01$, and the cubic δ phase with $x \approx 1.0$. This sample is a good example of how certain TMN growth conditions can lead to multiple crystalline phases coexisting in a single film. Increasing the growth temperature to 750°C leads to the appearance of predominantly cubic δ-NbN$_x$.
δ-NbNₓ peak shifting to larger angles and the appearance of the tetragonal γ phase with \( x \sim 0.80 \), consistent with less N incorporation in the film. Increasing the substrate temperature further leads to the appearance of a peak to the right of the 6H-SiC peak that is consistent with the hexagonal β-Nb₂N₃ phase.\(^{[17]}\) This change in phase behavior with increasing temperature is similar to previous reports on pulsed-laser or sputter-deposited NbNₓ materials, wherein the phase obtained can be a strong function of the growth temperature (at least in the cases when the Nb and N\(^{x} \) fluxes are not carefully matched).\(^{[48,49]}\) Single-phase NbNₓ—either [111]-oriented cubic δ-NbNₓ or [0001]-oriented hexagonal β-Nb₂N₃—is obtained at growth temperatures between 775 and 850 °C for these flux conditions. At 900 °C, the higher-angle NbNₓ peak diminishes significantly and trace evidence of another lower-angle NbNₓ phase begins to appear, indicating a loss of phase purity.

### 3.5. Chemical Composition by XPS/RBS/SIMS

The chemistry of TMNs is quite rich and complex compared with most semiconductors, so it is important to be able to quantify the chemical composition of the epitaxial TMN films. Also, while symmetric XRD measurements are commonly used for crystalline phase determination, it is important to recall that the NbNₓ and TaNₓ lattice constants vary with nitrogen content. In addition, the potential exists for lattice and thermal mismatches to introduce strains in the heteroepitaxial film. As a result of these factors, the XRD peak positions can vary from film to film without concurrent changes in crystalline phase.\(^{[50]}\) We have applied a variety of techniques to selected TMN films to quantify the composition and bonding in the films and to correlate those findings with XRD measurements.

Ex-situ XPS measurements were made either with a Thermo Scientific K-Alpha system\(^{[39]}\) or with an XPS system from Staib Instruments.\(^{[51]}\) Representative data are shown in Figure 7 for a 100 nm-thick NbNₓ film.\(^{[49]}\) Figure 7 shows the measured Nb 3d and N 1s XPS spectra taken after 1 keV low-current Ar-sputter cleaning of the air-exposed surface. The deconvoluted N 1s spectrum shown in the lower graph still shows evidence of oxygen contamination, so the sputter cleaning was insufficient to completely remove the native oxide. In addition, ex-situ XPS Ar-sputter cleaning can preferentially etch N compared with Nb atoms, changing the measured N/Nb ratio. Recognizing these nonidealities in the measurements, the binding energy of the single Nb 3d 5/2 peak shown in the upper graph is located at 202.8 eV, which lies between the previously reported values for δ-NbN(203.5–203.8 eV) and Nb metal (202.2 eV).\(^{[52]}\) In addition, the difference between the binding energies of the Nb 3d and N 1s peak is 194.5 eV, consistent with previous reports for NbNₓ films.\(^{[49]}\) Analyzing the total Nb 3d area relative to the total N 1s area obtained using standard techniques gives a Nb/N atomic ratio of 1.8 (\( x = 1/1.8 = 0.56 \)).

Similar ex-situ XPS measurements of the 43-nm-thick TaNₓ / 6H-SiC film after Ar-sputter cleaning (not shown) give a Ta content of 61–63 atomic percent (at%) (depending on the etch conditions) and a TaNₓ atomic ratio x-value of 0.59–0.64, indicating that this is an N-rich hexagonal γ-Ta₂N film or an N-lean hexagonal δ-TaN film.

![Figure 7](image.png)

Figure 7. Ex-situ XPS measurements of a 100-nm-thick NbNₓ film after low-energy sputter cleaning. Reproduced with permission.\(^{[49]}\) Copyright 2015, IOP Publishing.

Selected TMN films were also characterized by RBS and SIMS (not shown). In general, the films were uniform with less than 1 at% contamination by Nb in Ta and Ta in Nb. The Nb and Ta cross contamination was likely principally from the source materials used in the e-beam evaporator. The TMN films grown using the growth conditions described earlier and characterized to date have been N-lean cubic δ-NbNₓ and N-rich hexagonal γ-Ta₂N (or N-lean hexagonal δ-TaN), consistent with the XRD and XPS results.

### 3.6. Cross-sectional Transmission Electron Microscopy (XTEM)

High-quality XTEM measurements of representative samples are an invaluable tool for the identification and verification of hexagonal β-Nb₂N₃, γ-Ta₂N, or δ-TaN epitaxial phases. For the NbNₓ case, the complexity of the Nb–N phase diagram and the fact that several stable phases can coexist (some with overlapping compositions) can make phase identification difficult unless XTEM measurements are available. For the TaNₓ case, there is in addition a lack of reported data on the epitaxy of this material to serve as a reference for comparison.

Figure 8 shows the a) XTEM measurements and b) symmetric XRD measurements of an NbNₓ sample intentionally grown with a high Nb/N\(^{x} \) ratio (Nb ∼ 2.4 nm s\(^{-1} \), N\(^{x} \) ∼ 1.8 nm s\(^{-1} \)). As shown by the red overlaid squares, at least two phases are present. By comparing the atomic stacking sequences between the XTEM image and the ball-and-stick models, and examining the 2D fast Fourier transforms (FFTs) of the selected areas in the image, the grains can be identified as (1) [0001]-oriented hexagonal β-Nb₂N₃ (2) [111]-oriented cubic δ-NbNₓ and (3) tentatively identified...
overlapping [111]-oriented cubic $\delta$-NbN$_x$ grains with a modulo-60° in-plane rotation between them. Comparison of the XTEM image with the XRD measurements (and published data) allows us to identify the right-most TMN peak at $\theta = 77°$ in Figure 8b as corresponding to the 0004 reflection of hexagonal $\beta$-Nb$_2$N; and the peak just to its left at $\theta = 75.8°$ as corresponding to the 222 reflection of cubic $\delta$-NbN$_x$. Note that the first-order NbN$_x$ XRD peaks at $\theta = 36.25°$ are not separately resolved, so for this film it was important to extend the XRD measurement out to higher 2θ angles to access 2nd order peaks and increase their separation. Finally, in the XTEM image, note the sharp transition between the top hexagonal $\beta$-Nb$_2$N interface and the bottom of the [111]-oriented cubic $\delta$-NbN$_x$ layer at the surface. The cause of the phase change near the surface of the NbN$_x$ film is not yet clear and is under investigation.

Figure 9a shows a representative XTEM micrograph of the 43-nm-thick TaN$_x$/SiC sample. The TaN$_x$ film is uniform and single-phase except for isolated in-plane defects, and there is a sharp interface between the TaN$_x$ film and the SiC substrate. A selected-area FFT (the gold square of the left image) yields a rectangular grid pattern of spots for this imaging orientation, indicating the TaN$_x$ is hexagonal-symmetry crystalline material. Figure 9b shows an enlargement of the image on the left with CrystalMaker ball-and-stick models of hexagonal $\gamma$-Ta$_2$N and wurtzite $\delta$-TaN overlay the image and shows excellent agreement for both models, indicating the hexagonal phase is not uniquely determined yet. To date, using the N-rich...
growth conditions described earlier, a hexagonal TaN<sub>x</sub> phase has been dominant in our MBE-grown TaN<sub>x</sub> films, but identification of the particular hexagonal phase in this film is still in progress.

3.7. Electronic and Superconducting Properties of MBE-Grown TMNs

Cubic δ-NbN<sub>x</sub> is a well-known superconductor with superconducting transition temperatures (T<sub>c</sub>) as high as ≈17 K. The T<sub>c</sub> for δ-NbN<sub>x</sub> varies with the material quality and with the N/Nb atomic ratio “x”, with higher T<sub>c</sub> generally being found near x = 1.0. The T<sub>c</sub> for several representative MBE-grown cubic δ-NbN<sub>x</sub>/SiC epitaxial films is shown in Figure 10 along with representative published data for sputtered cubic δ-NbN<sub>x</sub> films. The T<sub>c</sub> of 16.7 K for the 50-nm-thick MBE-grown film is higher than the published results and indicates that improvements in the T<sub>c</sub> of thinner MBE-grown films can be expected with further optimization of the MBE growth conditions. There is a common fall-off in T<sub>c</sub> with decreasing thickness for very thin films. Modeling by Kang et al. indicates that the fall-off in T<sub>c</sub> is best described by an electron wave leakage model (red line in the figure).

Other important superconducting properties include the mean-free-path, coherence length, residual resistivity ratio, electron density and mobility, and the magnetic properties of the materials. Table 1 gives a brief summary of some of these properties for two MBE-grown cubic δ-NbN<sub>x</sub>/SiC epitaxial films. Note that even at 5 nm thickness, the T<sub>c</sub> of 6.41 K is substantially above the liquid helium temperature of 4.2 K. Also note that the coherence length of ≈10 nm in these two films is approximately double that of the typically cited value for cubic δ-NbN<sub>x</sub>. It is clear that MBE can be used to grow high-quality epitaxial superconducting NbN<sub>x</sub>. A more detailed discussion of these parameters and the magnetic properties of these MBE-grown films is presented by Yan et al.

Hexagonal TaN<sub>x</sub> has been reported for decades to be either non-superconducting or to have a T<sub>c</sub> below 1.5 K. Figure 11 shows the measured T<sub>c</sub> for the MBE-grown 43-nm-thick epitaxial hexagonal TaN<sub>x</sub> film is ≈1.25 K. Although this T<sub>c</sub> is too low for many superconducting device applications, being below the liquid He temperature, there are applications such as superconductor/normal-metal/superconductor (S–N–S) Josephson junction devices where high-quality epitaxy of the entire structure would be appealing and NbN<sub>x</sub>/Ta<sub>2</sub>N/NbN<sub>x</sub> or other TaN<sub>x</sub>-based structures may find applicability. For example, the AC Josephson effect using S–N–S junctions has been proposed as a programmable voltage standard.

![Figure 10](image_url) Measured superconducting transition temperature for three MBE-grown NbN<sub>x</sub> films on SiC compared to measurements and modeling by Kang. The 50-nm-thick MBE-grown NbN<sub>x</sub> layer T<sub>c</sub> is 16.7 K and indicates the high quality of the film. Kang’s results indicate that further improvements in the T<sub>c</sub> of thinner MBE-grown layers can be expected with further growth optimization.

![Figure 11](image_url) Measured superconducting transition temperature for 43-nm-thick TaN<sub>x</sub> layer grown by MBE on 6H-SiC. The T<sub>c</sub> = 1.25 K. This is the first reported measurement of the T<sub>c</sub> of hexagonal TaN<sub>x</sub>.

### Table 1. Selected properties of MBE-grown TMN superconductors.

<table>
<thead>
<tr>
<th>Property</th>
<th>Symbol</th>
<th>5 nm NbN&lt;sub&gt;x&lt;/sub&gt;</th>
<th>35 nm NbN&lt;sub&gt;x&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sheet resistance (Ω/□)</td>
<td>R&lt;sub&gt;sh&lt;/sub&gt;</td>
<td>107.9</td>
<td>9.8</td>
</tr>
<tr>
<td>Carrier concentration (10&lt;sup&gt;23&lt;/sup&gt; cm&lt;sup&gt;−3&lt;/sup&gt;)</td>
<td>n&lt;sub&gt;1D&lt;/sub&gt;</td>
<td>2.1</td>
<td>2.3</td>
</tr>
<tr>
<td>Electron Hall mobility (cm&lt;sup&gt;2&lt;/sup&gt; Vs&lt;sup&gt;−1&lt;/sup&gt;)</td>
<td>μ</td>
<td>0.54</td>
<td>0.93</td>
</tr>
<tr>
<td>Mean free path (Å)</td>
<td>l&lt;sub&gt;mfp&lt;/sub&gt;</td>
<td>6.6</td>
<td>11.6</td>
</tr>
<tr>
<td>Residual resistivity ratio</td>
<td>RRR</td>
<td>1.50</td>
<td>1.86</td>
</tr>
<tr>
<td>T&lt;sub&gt;c&lt;/sub&gt; (Resistance)</td>
<td>T&lt;sub&gt;c&lt;/sub&gt;</td>
<td>6.41</td>
<td>9.26</td>
</tr>
<tr>
<td>T&lt;sub&gt;c&lt;/sub&gt; (Magnetometry)</td>
<td>T&lt;sub&gt;c&lt;/sub&gt;</td>
<td>6.23</td>
<td>9.36</td>
</tr>
<tr>
<td>Coherence length (nm)</td>
<td>ξ</td>
<td>10.56</td>
<td>10.06</td>
</tr>
<tr>
<td>[N]/[Nb]</td>
<td>x</td>
<td>0.88</td>
<td>0.75</td>
</tr>
</tbody>
</table>
4. III-N Semiconductor/Superconductor Epitaxial Heterostructures on SiC

Although the lattice-mismatch between NbN<sub>x</sub>/TaN<sub>x</sub> and III-N semiconductors materials can be larger than that to SiC, it is still possible to grow high-quality epitaxial III-N heterostructures on the TMNs. Integration of epitaxial buried superconducting ground planes with III-N devices could ease fabrication of low-loss microwave transmission lines and serve as a prototype for ground planes for Josephson junction arrays that are being contemplated as practical voltage standards. In addition, the different chemistry of TMNs compared with III-N semiconductors enables the possibility of strongly selective etching and epitaxial lift-off and transfer of III-N devices from the host substrate to other substrates that may offer better thermal conductivity or opportunities for heterogenous device integration. However, the hexagonal III-N materials and the TMNs have different crystal structures as their space groups differ. In particular, III-N materials are polar (i.e., they lack inversion symmetry) so that the metal-polar and nitrogen-polar faces of the <sup>+</sup>[0001]-oriented crystals are different. In contrast, the cubic and hexagonal phases of NbN<sub>x</sub> and some hexagonal phases of TaN<sub>x</sub> have inversion symmetry so the <sup>+</sup>-[111]-faces of the cubic phases are equivalent as are the <sup>+</sup>-[0001]-faces of the hexagonal phases. This means that one must carefully consider the atomic alignment of the polar/nonpolar interfaces in heterostructures comprised of III-N semiconductors and TMNs.

Figure 12 shows a simple ball-and-stick model of interfaces between TMNs and the III-N semiconductors of interest. It is well known that the cohesive energy increases rapidly as the interatomic distance decreases from the equilibrium value. As such, we expect (to first order) that SiC and III-N materials have closer-to-equilibrium atomic stacking on TMNs (as indicated by the blue arrow) when the epitaxial interface is grown N-polar up than when it is grown III-polar up (indicated by the red arrow). In other words, there is less bond distortion and lower cohesive energy when the cation separation across the interface is similar to the bulk value. Similarly, TMNs have closer-to-equilibrium atomic stacking on Si-face or III-polar material than on C-polar or N-polar material. (To date, attempts at MBE growth of high-quality TMNs on C-polar SiC have been unsuccessful.) This interfacial stacking model applies whether the TMN is the [111]-oriented cubic phase or the [0001]-oriented hexagonal phases. The polarity of the III-N semiconductor on the TMN can be changed to metal-polar in the usual way through the use of carefully tailored nucleation layers.

Another complication in the formation of heteroepitaxial junctions between TMNs and III-Ns is that the cubic [111]-oriented...
TMNs can suffer from rotational twins and consequent formation of incoherent grain boundaries. Also, as Sands et al. point out, any differences in symmetry between heterojunction materials will, in general, lead to the formation of extended defects in the lower-symmetry material.[2] These grain boundaries can lead to the formation of threading dislocations and other extended defects that can adversely impact electronic and optical devices made from these materials. Although it has not been a focus of this work, it is expected that twinning in the cubic TMNs can be reduced or eliminated by using the same types of optimizations as used for the growth of twin-free 3C-SiC on 4H-SiC (namely through control of the surface step density and orientations as used for the growth of twin-free 3C-SiC on 4H-SiC).

High-quality epitaxial AlN layers have been grown in situ by MBE on NbN_x and TaN_x and have properties similar to those grown directly on SiC.[67,68] For example, Figure 13 shows the symmetric XRD data measured for a 200-nm-thick AlN/100-nm-thick δ-NbN_x/6H-SiC heterostructure grown by MBE. The peaks are sharp and in the expected positions for the [111]-oriented δ-NbN_x and hexagonal AlN phases. This result indicates that the high quality of the δ-NbN_x is preserved even after AlN overgrowth, and that high-quality AlN can be grown epitaxially on [111]-oriented δ-NbN_x.

Figure 14 shows a representative XTEM micrograph of a similar AlN/30-nm-thick δ-NbN_x/6H-SiC sample.[67] The δ-NbN_x/SiC interface is sharp as is the AlN/δ-NbN_x interface. Unfortunately, the resolution in this particular image was too low to perform FFTs to verify the δ-NbN_x crystalline phase.

Electrical measurements of metal/AlN/δ-NbN_x/SiC capacitors showed that the epitaxial AlN on δ-NbN_x is of high electrical quality as well.[68] Vertical breakdown fields exceeding 5.5 MV cm^{-1} were measured on simple MIM devices without any contact-edge termination optimizations.

Thick GaN layers can also be grown on TMNs with the expected properties. Figure 15 shows a summary of a growth experiment in which GaN was grown by MBE for 24 h on AlN/NbN_x to see the effect of long temperature exposure and overgrowth on the 54-nm-thick MBE-grown NbN_x film and to measure the GaN properties.[63] In this case, the GaN is Ga-polar as the polarity was flipped from N-polar to Ga-polar by growing a low-temperature (LT) AlN layer on the NbN_x film before growing the GaN. Post-growth AFM images show that the film is very smooth, with atomic-step terraces and an rms roughness of 0.24 nm. The XRD data shows Pendellösung fringes from the sharp NbN_x/SiC interface, and an intense and sharp GaN peak. The FWHM of the XRD rocking curve of the 0002 GaN peak is 45 arc-sec (not shown). Fitting of the optical reflectance oscillations shows the expected GaN bandgap feature and gives the expected growth rate. Although we expect stress in the GaN layer as a consequence of the thermal expansion mismatch between the GaN and the AlN/NbN_x/SiC layer stack, these results show that the stress is manageable (only low levels of cracking were seen via optical microscopy) even for thick GaN layers. This experiment shows that NbN_x tolerates long-duration high-temperature MBE growth cycles and that high-quality Ga-polar GaN can be grown epitaxially on NbN_x.

Finally, N-polar and Ga-polar high electron mobility transistor (HETM) layers can be grown on epitaxial TMNs by MBE and achieve electrical quality comparable with those structures grown directly on SiC. Figure 16a shows a summary of N-polar GaN/AlGaN HEMTs grown on NbN_x.[61] The structure includes a 30-nm-thick NbN_x layer, a 100-nm-thick AlN layer, and a 1.3-μm-thick GaN buffer, followed by a 30-nm-thick Al_{0.4}Ga_{0.6}N barrier and a 30-nm-thick GaN channel. A representative dark-field cross-sectional scanning transmission electron micrograph (STEM) of the layers shows the abrupt interfaces and the usual reduction of the threading dislocation density in...
the GaN as the layer thickness increases. The XRD indicates the layers are all present with high quality, and this is reflected in the DC characteristics of the fabricated HEMTs. The Hall effect mobility is 1375 cm² V⁻¹ s⁻¹, and both of these values are comparable to those obtained for a similar HEMT structure grown directly on SiC. The HEMT open-channel current exceeds 1 A mm⁻¹, and good pinch-off is obtained. In addition, breakdown to the buried NbNₓ is not observed until the drain voltage exceeds 90 V (≈7 × 10⁵ V cm⁻¹). Figure 16b shows an early Ga-polar HEMT structure consisting of a 45-nm-thick LT AlN layer on a 50-nm-thick NbNₓ layer. The structure then includes a 1.2-μm-thick GaN buffer layer and a 25-nm-thick Al₀.₂₈GaN barrier. Although the XRD indicates the layers are of high quality, the carrier mobility is low at 995 cm² V⁻¹ s⁻¹, thereby limiting the transistor current and performance. Further optimization of the Ga-polar GaN growth on TMNs is expected to result in higher channel transport performance that matches or exceeds the aforementioned N-polar results.

The N-polar HEMTs on NbNₓ discussed earlier were recently studied at low temperature and at high magnetic fields to learn more about their electronic and magnetic properties. Most of the measurements were made using a Quantum Design PPMS system. As part of that work, electrical contact was created between the N-polar HEMT source and the buried NbNₓ layer to use the NbNₓ as an electrical load. As seen in Figure 17, the circuit functions as expected. The HEMT has good operating characteristics at low temperature, and as the temperature is swept through the T_c of this NbNₓ film (7.7 K), the NbNₓ changes from a normal conductor to a superconductor. When operated at 5 K, as the dissipated electrical power in the device increases and raises the NbNₓ temperature above T_c, the I–V characteristics show a negative differential resistance when the metal changes from a superconductor to a normal metal. This is the first time such a phase change has been observed in epitaxial III-N/superconductor structures, and this indicates the promise of epitaxial integration of TMNs with III-N transistors for novel superconducting device and circuit applications.
5. Conclusion

The benefits of the epitaxial integration of cubic $\delta$-NbN$_x$, hexagonal $\beta$-Nb$_2$N, and hexagonal TaN$_x$ with SiC and group III nitride semiconductors have been discussed. These materials are nearly lattice-matched and can be grown by MBE to yield high-quality films as shown by a variety of characterization techniques. Direct epitaxy of III-N semiconductor materials, including GaN HEMTs, has been demonstrated on superconducting cubic $\delta$-NbN$_x$, and the device characteristics show the promise of this unique epitaxial semiconductor–superconductor materials system.
Acknowledgements
This work was supported by the Office of Naval Research (Dr. Paul Maki), with additional support at Cornell from the National Science Foundation. The authors appreciate the use of L.B. Ruppall's Lake Shore Cryotronics probe station for some of the Tc measurements at NRL.

Conflict of Interest
The authors declare no conflict of interest.

Keywords
molecular beam epitaxy, superconductors, transition metal nitrides, transmission electron diffraction, x-ray diffraction

Received: August 19, 2019
Revised: October 2, 2019
Published online: November 11, 2019