

Plasma-Assisted MOCVD Growth of Superconducting NbN Thin Films Using Nb Dialkylamide and Nb Alkylimide Precursors**

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Niobium nitride (NbN) thin films are of considerable interest due to their excellent mechanical and chemical stability, as well as having useful superconducting properties. Regarding the latter, NbN has a relatively high critical temperature (T_c), critical field (H_{c2}), and critical current density (J_c), and has a refractory nature. It is therefore a promising candidate for superconducting microelectronics applications such as superconducting quantum interference devices (SQUIDs), radio frequency (rf) filters, antennae, and sensitive infrared (IR) sensors.^[1–4] Thus far, NbN thin films have been grown primarily by physical vapor deposition (PVD) techniques, including sputtering,^[5–8] pulsed laser deposition (PLD),^[9,10] and molecular beam epitaxy (MBE).^[11] Among these, reactive sputtering has been most frequently employed, and NbN thin films with T_c values approaching 16 K have been grown by optimized reactive sputtering. However, superconducting NbN film growth mechanisms have not been fully elucidated; moreover, optimal growth conditions are highly growth system specific, and the growth reproducibility of high-quality films is not yet satisfactory.

CVD is a widely utilized technique in film growth research as well as in industrial-scale production. Although the attractions of CVD include excellent step coverage, adaptability to large-scale growth processes, and relatively simple apparatus, relatively little work has been carried out on NbN_x thin films.^[12,13] Understanding and perfecting NbN CVD processes would better define the parameters required for large-scale NbN CVD, as well as for nitride CVD in general. Additional knowledge would also lead to

better understanding of phase transformations as well as nitride CVD nucleation and growth processes. In this contribution, a pulsed source, plasma-assisted, low-pressure MOCVD process (POMBE),^[14] using a hydrazine plasma, is implemented for the first time to grow high-quality, superconducting NbN thin films at low temperatures. Paramount to efficient MOCVD processes is the availability of volatile metal–organic precursors, and an understanding of the structure/property relationships between precursors and the resultant films. In this report, two different types of metal–organic precursors (a previously described niobium(IV) dialkylamide and a new pentavalent alkylimide) are compared in the growth of highly oriented B1–NbN superconducting thin films on MgO(001) ($a = 4.213 \text{ \AA}$; 4% lattice mismatch) substrates. Details of film growth, microstructure, and superconducting properties, as well as the preparation of a new series of volatile Nb alkylimido precursors are described.

To establish the viability of POMBE for NbN film growth, experiments were first carried out with the known Nb dialkylamide, Nb(NEt₂)₄ (**1**), prepared and purified according to the literature,^[15] using a hydrazine plasma as the nitrogen source. NbN films, grown at temperatures ranging from 350 °C to 800 °C, were analyzed by X-ray diffraction (XRD), which reveals that higher growth temperatures produce greater film crystallinity. This enhanced crystallinity can be correlated with higher superconducting critical temperatures, which are only distinct in films grown at substrate temperatures above 600 °C. XRD results for a NbN film grown at 750 °C reveal highly a -axis oriented film growth under these conditions (see Fig. 1A). For NbN films grown at temperatures above 700 °C, the typical full width at half maximum (FWHM) of ω rocking curve scans of the NbN(200) reflections (inset, Fig. 1A) are between 0.5° and 1.2°, also suggesting that the films are highly textured.

The rock salt superconducting δ phase of NbN has a face-centered cubic lattice (B1 structure) with $a = 4.392 \text{ \AA}$ (JCPDS-38-1155). Nitrogen atoms are located in the octahedral interstitial sites of the Nb atom sublattice. According to the NbN phase diagram,^[16] the superconducting δ phase is metastable at 25 °C, the presence of the γ and ϵ phases is possible, and thus the lattice of the δ phase may be distorted. It has also been reported that the NbN lattice parameter is sensitive to the Nb/N ratio.^[17] Our results show that critical temperatures can be correlated with the lattice parameters of the superconducting NbN films. Indeed, the film with the highest T_c has a lattice parameter of 4.395 Å, which best corresponds to JCPDS data. These results suggest that the superconducting properties of POMBE-derived NbN films are sensitive to phase purity and stoichiometry, as has been reported for sputtered NbN thin films.^[17]

Impurities can have significant effects on the superconducting properties of NbN films. From Auger electron spectroscopy (AES) studies, the principal impurities in the present NbN films are found to be C (probably from the

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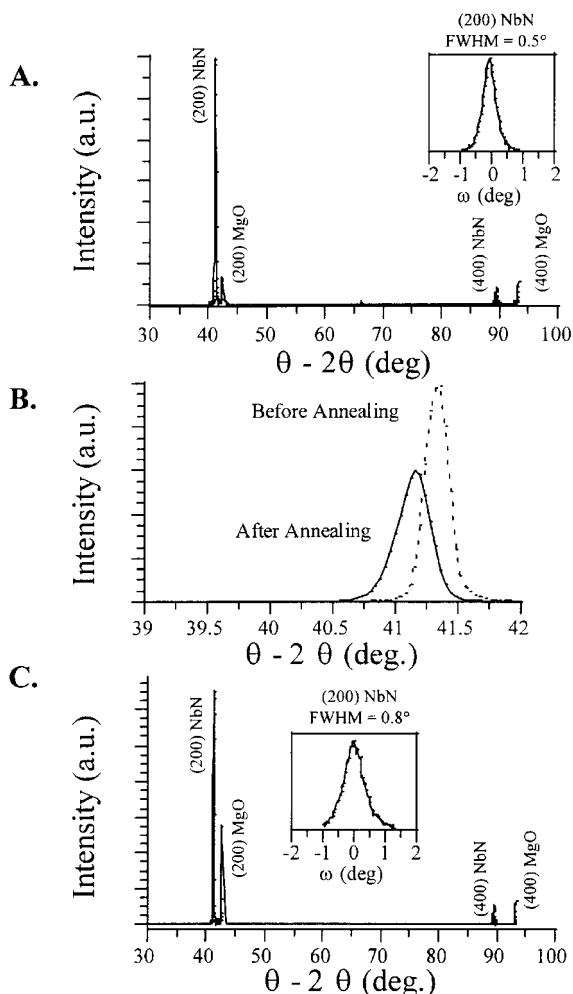


Fig. 1. A) XRD θ - 2θ and ω (inset) scans of POMBE-derived NbN thin films grown in-situ on MgO(001) at 750 °C using dialkylamide precursor **1**. B) Displacement of the NbN(200) reflection in the θ - 2θ scan after annealing under H₂. C) XRD θ - 2θ and ω (inset) scans of NbN thin films grown under the conditions described above using alkylimide precursor **2b**.

ligands) and O (probably from traces of H₂O in the N₂H₄); however, no significant influence of C impurities on T_c is observed. It has been reported that introducing C sources into the reaction gas mixture slightly increases T_c values of sputtered NbN films, presumably via NbN_{1-x}C_x alloy formation.^[18] Table 1 shows a series of AES measurements on the POMBE-derived NbN films exhibiting differing T_c values. Note that O impurities induce a considerable degradation of T_c . This probably results from the niobium oxide defect phases.^[19] Upon annealing a POMBE-derived NbN film at ~1000 °C in H₂ for 2 h, T_c is increased from 6 K to 12.9 K. Representative inductive T_c data are shown in Fig-

Table 1. AES assays of POMBE-derived NbN films

Sample	Precursor	Substrate Temp. [°C]	% O	% C	T_c [K]
1	1	750	3.2	11.0	9.25
2	1	750	3.5	8.8	7.53
3	1	550	13.5	10.0	< 4.2
4	2b	750	11.0	8.8	6.5

ure 2. Due to the instability of δ -NbN, facile transformations to the γ -Nb₄N₃ + ϵ -NbN phases (accompanied by N loss) can occur.^[20] Furthermore, it is known that vacancies in δ -NbN can be removed by annealing in H₂, thus increas-

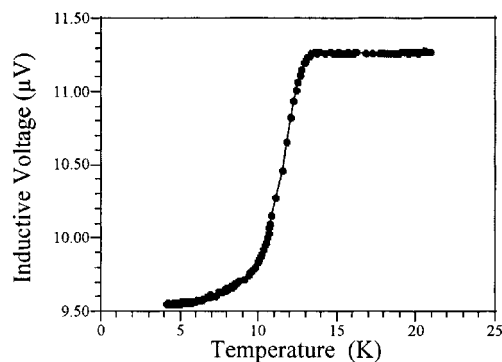
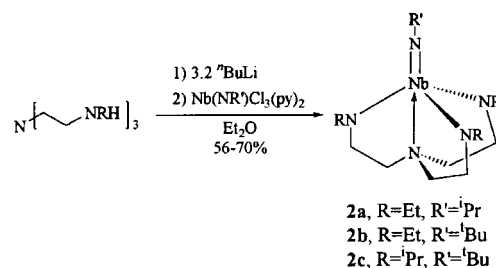


Fig. 2. Inductive measurement of T_c for an H₂-annealed NbN film grown using Nb(NEt₂)₄ as the precursor.

ing T_c and the lattice parameter. High-temperature H₂ annealing may also reduce O contamination, via removal as H₂O. The present observed change in lattice parameter can be calculated from the XRD data of Figure 1B, and indicates an increase in cell constant from 4.369 Å to 4.389 Å upon annealing. The latter value is close to that reported in the JCPDS data file.

Once the conditions were optimized for POMBE growth of superconducting NbN films, the effect of the metal-organic precursor was investigated. It has been suggested^[21,22] that alkylimides may be efficacious nitride CVD precursors due to the presence of a strong metal-nitrogen bond, and a Ta alkylimide was previously used as a single source to deposit polycrystalline TaN via MOCVD.^[23] To test this hypothesis, a new volatile Nb imide (devoid of ligands containing O, Si, or heavier halides) was sought, the importance of this characteristic having been demonstrated by results regarding impurity effects on the T_c (vide supra). The synthesis of complexes **2a-c** is achieved via the straightforward reaction of tris-(aminoethyl)amine trilitium salts^[24,25] (Scheme 1) with niobium alkylimido trichlorides.^[26]

The pure products are obtained after sublimation as crystalline solids, the melting points of which are highly dependent on the nature of R and R'. Chelating triamido-amides or azatrane ligands were selected over simple dial-



Scheme 1.

kylamides to enhance thermal stability. Complex **2b** was characterized by single-crystal XRD, with satisfactory NMR and elemental analyses obtained for the series (see Experimental for details).

The solid-state structure of **2b** (Fig. 3)^[27] reveals a distorted tetrahedral geometry with three dissimilar Nb–N bond lengths: a short double bond [1.791(2) Å], three sin-

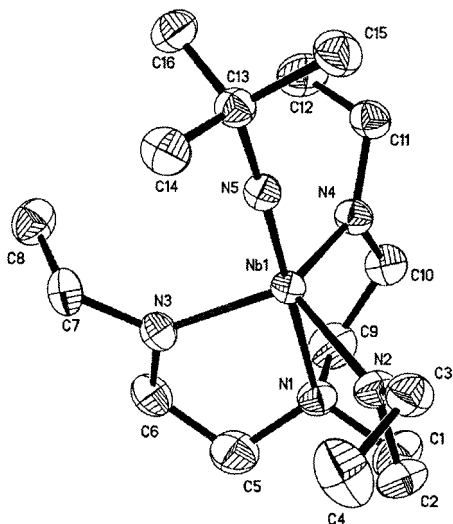


Fig. 3. ORTEP drawing of the $[N(CH_2CH_2NEt_3)_3]Nb=N'Bu$ (**2b**) molecular structure with atomic labeling scheme. H atoms are omitted for clarity, and the ellipsoids are drawn at the 30% probability level. Relevant bond distances [Å] and angles [°] are: Nb(1)–N(5) = 1.791(2), Nb(1)–N(4) = 2.027(2), Nb(1)–N(3) = 2.030(2), Nb(1)–N(2) = 2.038(2), Nb(1)–N(1) = 2.358(2); N(5)–Nb(1)–N(4) = 103.00(7), N(3)–Nb(1)–N(2) = 115.71(8), N(5)–Nb(1)–N(1) = 179.15(7), C(13)–N(5)–Nb(1) = 177.59(5).

gle bonds averaging 2.032(2) Å, and a long dative bond [2.358(2) Å]. The short Nb–N5 imide bond length and the nearly linear Nb–N5–C13 angle [177.59(15)°] suggest an extremely strong interaction between the Nb center and the imido N, approaching triple bond character. The N1–Nb–N5 vector is also nearly linear at 179.15(7)°.

Using the optimal conditions determined above for NbN POMBE growth with precursor **1**, phase-pure, highly textured films were grown at 750 °C using precursor **2b** (see Fig. 1C). From series **2a–c**, complex **2b** was chosen because of the relatively high synthetic yield and low melting point, 95 °C, which is sufficiently low to provide a liquid precursor under normal growth conditions yet not too low to impede bubbler loading. T_c and AES measurements of NbN films grown at 750 °C suggest these films may be slightly lower in quality than those deposited using **1**. The highest T_c obtained was 6.77 K for an as-grown film, which was enhanced to 7.97 K upon H_2 annealing. The lattice parameters are 4.366 Å and 4.381 Å for the as-grown and H_2 -annealed films, respectively. This annealing-related shift of the lattice parameter is similar to that found in the Nb(NEt₂)₄-derived films described above. The AES for the pre-annealed sample (Table 1) reveals a slightly higher level

of O contamination for the film grown with **2b** than that grown with **1** at the same temperature. Another striking difference in these two samples is morphology. The NbN film grown using **2b** has a much smaller average grain size (Fig. 4), which may be another cause of the diminished T_c .

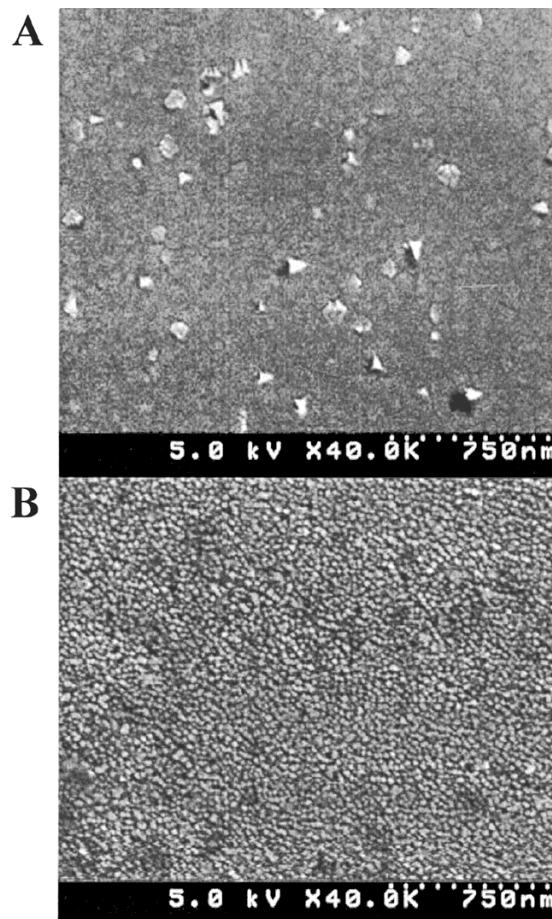


Fig. 4. Scanning electron microscopy (SEM) images of POMBE-derived NbN films grown under the same conditions using the precursors: A) Nb(NEt₂)₄, B) new Nb imide **2b**.

In summary, we report the first example of superconducting NbN thin-film growth using metal–organic precursors and POMBE, a pulsed plasma-assisted CVD technique, for the *lowest NbN superconductor growth temperature yet achieved*. The T_c of the films grown using Nb(NEt₂)₄ is highly dependant on the lattice parameter and level of O impurities, both of which are governed by growth temperature and post-deposition annealing. The synthesis, characterization, and solid-state structure of a new Nb precursor containing a short Nb=N alkyimido bond is also reported, and NbN films are grown using this precursor. With either precursor, T_c is enhanced upon annealing in H_2 , a step proposed to reduce vacancies in the superconducting δ -NbN lattice. The highest T_c , 12.9 K, was achieved with an annealed film grown at 750 °C using Nb(NEt₂)₄ as the precursor.

Experimental

[Tris(amidoethyl)amine](imido)niobium(v) Complexes (**2a–c**): Representative procedure for **2b**. A 1 L round bottom Schlenk flask equipped with a magnetic stir bar and a rubber septum is charged with a tris(*N*-ethylaminoethyl)amine (0.037 mol, distilled and stored over molecular sieves) solution in 200 mL Et₂O, cooled to 0 °C, and treated with *n*-butyllithium (0.11 mol; 3.0 equiv.) via a syringe. The reaction mixture was warmed to room temperature, and refluxed for 2 h. The resultant solution was then added via a cannula to a suspension of Cl₃Nb=N⁺Bu(py)₂ [28] (0.037 mol) in 150 mL Et₂O, pre-cooled to –78 °C. The resulting brown suspension was next warmed to 78 °C and stirred for an additional 12 h. Volatiles were removed in vacuo, and the crude product extracted with pentane (3 × 50 mL) and filtered through a glass frit under N₂ into a Schlenk flask. The pentane was removed in vacuo, and pure **2b** obtained via sublimation (90 °C/10^{–4} torr) as a pale-yellow solid.

For 2a: 56 % yield; m.p. 37–40 °C; ¹H NMR (C₆D₆, 25 °C): δ 3.944 [d, 6 H, CH(CH₃)₂], 3.941 [q, 6 H, NCH₂CH₃], 3.098 [t, 6 H, CH₂CH₂], 2.351 (t, 6 H, CH₂CH₂), 1.334 [t, 9 H, NCH₂CH₃]. Anal. Calcd. for C₁₅H₃₄N₅Nb: C, 47.74; H, 9.08; N, 18.56. Found: C, 47.58; H, 9.19; N, 18.76.

For 2b: 70 % yield; m.p. 95 °C; ¹H NMR (C₆D₆, 25 °C): δ 3.967 [q, 6 H, NCH₂CH₃], 3.082 [t, 6 H, CH₂CH₂], 2.345 [t, 6 H, CH₂CH₂], 1.497 [s, 9 H, C(CH₃)₃], 1.316 [t, 9 H, NCH₂CH₃]. Anal. Calcd. for C₁₆H₃₆N₅Nb: C, 49.10; H, 9.27; N, 17.89. Found: C, 48.79; H, 9.14; N, 17.89.

For 2c: 67 % yield; m.p. 155 °C; ¹H NMR (C₆D₆, 25 °C): δ 4.933 [sept., 3 H, CH(CH₃)₂], 3.068 [t, 6 H, CH₂CH₂], 2.320 [t, 6 H, CH₂CH₂], 1.511 [s, 9 H, C(CH₃)₃], 1.312 [d, 18 H, CH(CH₃)₂]; Anal. Calcd. for C₁₉H₄₂N₅Nb: C, 52.64; H, 9.77; N, 16.16. Found: C, 52.38; H, 9.98; N, 16.30.

Film Growth: NbN films were grown in the previously described pulsed organometallic beam epitaxy (POMBE) reactor [14]. Prior to deposition, the reaction chamber was baked at 120 °C and pumped to a base pressure of 1 × 10^{–7} torr. The precursor reservoir was maintained at 85 °C for complex **1** and 135 °C for **2b**, with a He carrier flow rate of 5 sccm. Hydrazine (H₂NNH₂) was introduced directly to the reaction chamber through a leak valve. During deposition, substrates were maintained at 750 °C, and films grown in a hydrazine plasma at a total working pressure of ~7 mtorr. The substrates used in all growth experiments were cleaned with acetone and methanol immediately before being mounted on the substrate holder. Constituent phases, film orientation, and out-of-plane rocking curves were measured by XRD on a Matrix θ–2θ diffractometer with a monochromatic Cu Kα source. Lattice parameters were calculated from the XRD patterns. Film composition was assayed by scanning Auger spectroscopy on a Physical Electronics scanning Auger microprobe 590A. Film T_c values were measured by the inductive technique [29] using a single coil configuration. T_c is determined by the onset of drop in the inductive voltage, the magnitude of which is dependent on the film-coil space and not the sample quality.

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Self-Reducible Cu^{II} Source Reagents for the CVD of Copper**

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Copper thin-film materials are of great interest in the microelectronics industry for use as conducting layers in the manufacture of upper level metal interconnects, and for filling contact and via holes.^[1] The advantages of copper over other possible conducting materials, such as aluminum, include lower resistivity, improved electromigration resistance, and increased resistance to stress-induced voidage. Other well-known advantages related to device performance include greater speed, reduced cross-talk, and smaller RC time constants.

Copper thin films have been prepared by CVD using Cu^{II} complexes with β-acetoacetate, β-ketoiminate, or a β-diketonate such as Cu(hfac)₂.^[2] Upon introducing H₂ as

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