

# Fabrication of NbN/AlN superconducting multilayers

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Multilayers consisting of superconducting niobium nitride alternated with layers of insulating aluminum nitride have been fabricated using dc magnetron reactive sputtering. Under the proper conditions NbN can be produced in a (111) orientation and AlN in a (0001) orientation with an in-plane lattice mismatch of only 0.27%. Proper preparation of the aluminum target was necessary to ensure uniform deposition. X-ray diffraction and transmission electron microscopy verify the layered nature of these samples. Transport properties are studied as they relate to the structure of the system.

## I. INTRODUCTION

Niobium nitride is of current interest as a moderately high  $T_c$  (16 K), high  $H_{c2}$  (44 T) superconductor.<sup>1</sup> Because of its ability to tolerate radiation<sup>2</sup> and strain,<sup>3</sup> it has been proposed as a practical magnet material for future fusion work.<sup>4</sup> Potential applications of thin superconducting layers include films with two-dimensionally enhanced parallel critical fields,<sup>5,6</sup> important to magnet technology, and use as a base layer in Josephson tunnel junction technology.<sup>7</sup> Thin superconducting layers also allow the study of superconducting critical field anisotropy. NbN generally is fabricated by reactive sputtering (dc magnetron<sup>8</sup> or rf<sup>9</sup>) in which a metal is sputtered in the presence of a mixture of argon and reactive nitrogen; it can also be fabricated by ion beam deposition,<sup>10</sup> thin-film diffusion,<sup>11</sup> or chemical vapor deposition (CVD).<sup>12</sup> The microstructure, and hence many physical properties, of a superconductor can be altered by growth in a thin layer. A direct way of doing this is to insert alternate layers of a second insulating material such as aluminum nitride to prevent deleterious proximity effects. AlN can readily be prepared by rf sputtering,<sup>13</sup> dc sputtering,<sup>14</sup> CVD,<sup>15</sup> or dual ion beam deposition.<sup>10</sup> The latter method has also been used to prepare NbN/AlN/NbN sandwiches.<sup>10,16</sup>

In this paper we describe the fabrication of niobium nitride/aluminum nitride multilayers by dc magnetron sputtering of both compounds. Samples were prepared by optimizing sputtering gas partial pressures (6-mTorr Ar, 2-mTorr N<sub>2</sub>), substrate temperature (300 °C), and deposition rates (15-Å/s NbN, 6-Å/s AlN) until samples with the desired crystal orientation and superconducting critical temperature were achieved. Section II of this paper describes the material properties that make NbN/AlN an interesting system for study. Section III describes the experimental procedure and equipment used to produce high-quality samples. Section IV presents x-ray diffraction, transmission electron microscopy results, and transport measurements which relate to the structure of the samples that have been fabricated.

## II. MATERIAL PROPERTIES

NbN is a metal with a rock-salt structure and can be grown in a (111) orientation. Viewed along the [111] axis, NbN has a hexagonal in-plane lattice structure with alternating planes of niobium and nitrogen. The interatomic spacing in the niobium or nitrogen layers is given by  $a/\sqrt{2}$ , where  $a$  is the length of a unit cell of rock-salt NbN and is equal to 4.389 Å. This gives an in-plane spacing for NbN of 3.103 Å. AlN, a wide-gap (6 eV) semiconductor, has the wurtzite lattice structure. It is used in this study as a low-temperature insulating barrier to constrain NbN into thin layers. In its (0001) basal crystallographic orientation, AlN has an in-plane hexagonal structure with an in-plane spacing of 3.111 Å. Thus, the difference between the in-plane atomic spacings of NbN and AlN is only 0.27%; this difference should introduce very little strain at the interface. Although this would suggest that epitaxial layers should be achievable, epitaxy has not been experimentally confirmed and electron diffraction results show the samples to be polycrystalline.

The two compounds have nitrogen in common, which prevents the Nb and Al from reacting chemically at their interfaces. Both NbN and AlN have melting points above 2000 °C; therefore, interdiffusion of the layers is limited.

## III. EXPERIMENTAL METHOD

### A. Equipment

Multilayer films were prepared with two dc magnetron guns (Varian 5-in. S guns) equipped with 99.9% Nb and 99.999% Al targets, respectively, sputtering upward onto (10 $\bar{1}$ 0), (11 $\bar{2}$ 0) sapphire and (111) silicon substrates 10 cm above the target. No effect on film orientation was observed for the three substrates discussed in this paper. Each substrate was attached to a tantalum strip heater capable of temperatures up to 1000 °C. On the opposite side of the heater is fastened an identical sapphire substrate to which is attached a Chromel-Alumel thermocouple; in this way the actual substrate temperature is simulated. A multilayer specimen is prepared by alternately rotating the table over the Nb gun and the Al gun. Eight individual heaters, spaced symmetrically about a substrate table, with a movable shutter system allow a single substrate to be exposed until growth

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of the multilayer is completed. This substrate is then shielded and the next substrate is exposed. Eight samples of varied layer thicknesses can be prepared in this way under the same vacuum conditions.

The sputtering gases were monitored during deposition by a mass spectrometer which controlled the individual partial pressures to 0.1 mTorr by means of a feedback loop with piezoelectric valves connected to the gas sources. This was found to be important in controlling the nitrogen partial pressure, as a 0.6 mTorr variation of  $N_2$  partial pressure resulted in a 36% reduction in  $T_c$ . The sputtering rate of the guns was determined by use of quartz crystal monitors and verified with the help of profilometry, x-ray diffraction and transmission electron microscopy. The layer thicknesses could be varied by changing the speed of the stepping motor (controlled by an HP-86 computer) as it rotated the substrate table over the two sputtering guns.

The resistivity of the samples as a function of temperature was measured by a computer controlled closed-cycle refrigerator capable of measuring up to seven samples simultaneously. The temperature was determined by means of diode thermometers with NBS traceable standards.

## B. Deposition procedure

The films were deposited on substrates previously cleaned with Alconox, deionized water, and ethanol (for 10 min each) in an ultrasonic cleaner and then outgassed in vacuum for 20 min at 500 °C immediately before deposition. NbN is readily produced by reactive sputtering in an atmosphere of 6:1 argon to nitrogen. In order to avoid poisoning of the Al target by the process and in order to produce high-quality AlN, the nitrogen content was kept at the minimum level which still permitted the deposition of basally oriented AlN. The formation of AlN was also enhanced by increasing the substrate temperature to 300 °C. Once this minimum nitrogen partial pressure was determined, the NbN critical temperature was optimized by varying the niobium sputtering rate and the total argon and nitrogen sputtering pressure. Between runs, which consisted of depositing onto a single substrate, all substrates were shielded and the Al gun was sputtered clean in a pure argon environment for approximately 20–30 min in order to clear the nitrogen poisoning from the target surface. Approximately 20 min of AlN sputtering could then be carried out at a constant rate without risk of target poisoning. A typical multilayer consisted of 31 layers of AlN and 30 layers of NbN; in this way each NbN layer had essentially identical interfaces.

The typical base pressure of the system prior to admitting the sputtering gasses was  $1-2 \times 10^{-7}$  Torr. Samples were sputtered under a pressure of 6-mTorr argon (5–9's purity) and 2–3 mTorr nitrogen (5–9's purity), at a substrate temperature of 300 °C. A NbN gun voltage of 450 V and current of 7 A was used which resulted in a deposition rate of 15 Å/s. The AlN gun at a voltage of 350 V and 6.2 A had a rate of 6 Å/s.

Samples produced at other than optimum conditions could be annealed to increase the superconducting critical temperature. For instance, a nitrogen deficient sample annealed at 650 °C for 30 min at  $1 \times 10^{-6}$  Torr increased its

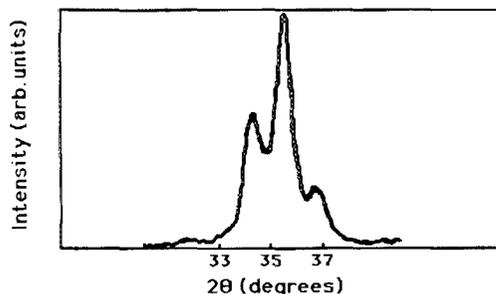


FIG. 1. High-angle scattering shows the characteristic satellite peaks due to superlattice modulation of NbN/AlN (45 Å/45 Å).

critical temperature from under 7 to 13 K. Since no change was observed in the x-ray diffraction scan of this sample, the increased  $T_c$  was probably due to vacancy filling in the sample.

## IV. CHARACTERIZATION

X-ray diffraction with  $CuK\alpha$  radiation clearly shows the composition modulation as evidenced by the appearance of high-angle crystalline superlattice peaks (Fig. 1). The typical full width at half maximum (FWHM) of the central peak was  $0.7^\circ$ , indicating a superlattice coherence length of  $\sim 70$  Å. The positions and the relative intensities of the peaks agree with a kinematic model simulation of the scattering.

Typically, 2–3 orders of small angle diffraction (Bragg scattering from the multilayer structure) were observed, as shown in Fig. 2. The near extinction of the  $n = 2$  peak is due to destructive interference in samples with equal NbN and AlN layer thickness. The FWHM of the  $n = 1$  peak was  $\sim 0.14^\circ$ ; the small angle rocking curve had an FWHM of  $\sim 0.05^\circ$ , with a shape similar to that observed earlier in the V/Ni system.<sup>17</sup>

Depending on the exact sputtering and vacuum conditions, it is possible to produce (111)-oriented NbN or NbN with both (111) and (200) orientations. Samples made under identical sputtering conditions but different NbN layer thicknesses exhibit a change in NbN orientation as a function of layer thickness (Fig. 3). Samples with thin NbN layers exhibit a predominantly (111) orientation, indicating that the AlN is forcing a (111) orientation on the NbN; whereas those with thicker NbN layers show a large fraction of (200) orientation.

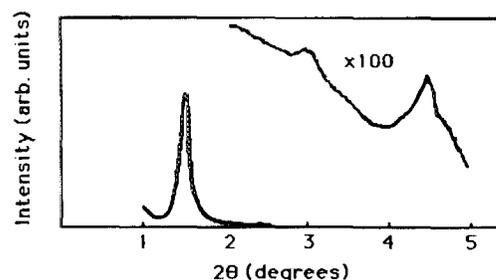


FIG. 2. Small angle scattering from a NbN/AlN (30 Å/30 Å) superlattice due to Bragg scattering ( $n = 1, 2, 3$ ) from the artificial periodicity.

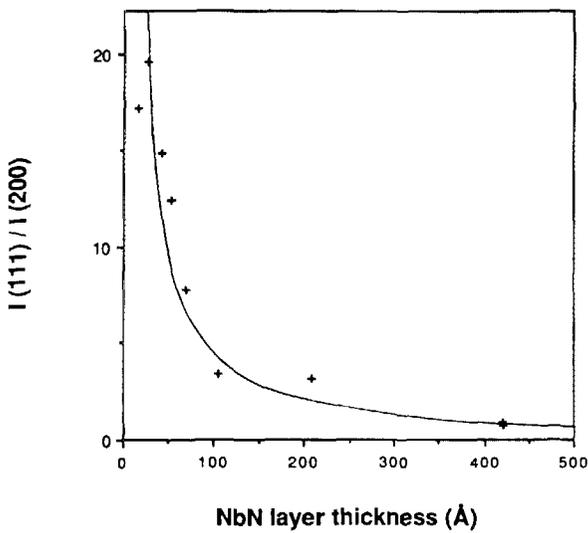


FIG. 3. Ratio of the x-ray intensities of the (111) and (200) reflections vs NbN layer thickness for equal layer thickness samples.

Figure 4 shows a transmission electron micrograph of a NbN/AlN multilayer on a silicon substrate using the microcleavage transmission electron microscopy technique developed earlier.<sup>18</sup> With this technique, microscopic wedges of the material are examined and the layer dimensions determined accurately from the point of the wedge (at the far left side of the photograph). The dark layers are NbN with a thickness of 40 Å and the lighter layers are AlN of thickness 102 Å; the total sample thickness is 815 Å. The contamination surface layer is an acetone residue left from sample cleaning and the parallel vertical lines are believed to be due to interference effects between crystallites at different depths within the sample.

The micrograph in Fig. 5 shows a sample with decreasing layer thicknesses of both AlN and NbN from bottom to top. As the thickness of the layers approaches 20–30 Å, the roughness becomes nearly equal to the layer thickness and consequently a degradation of the transport properties is expected.

Critical temperatures of the multilayer structures were approximately 80% of the thick-film value (16 K) for samples with NbN layer thickness greater than 80 Å, but degraded quickly for samples with thinner NbN layers [Fig. 6(a)]. This is consistent with the well known  $T_c$  suppression due to

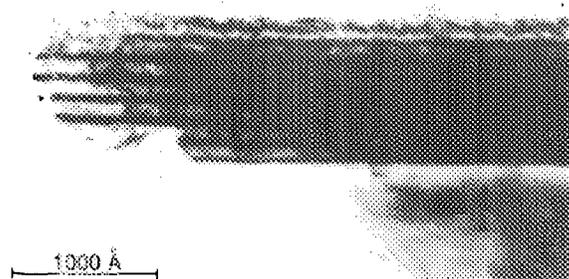


FIG. 4. Transmission electron micrograph of a NbN/AlN multilayer. The NbN (dark layers) thickness is 102 Å and the AlN (light layers) thickness is 40 Å. The silicon substrate is seen in the bottom right attached to the film.

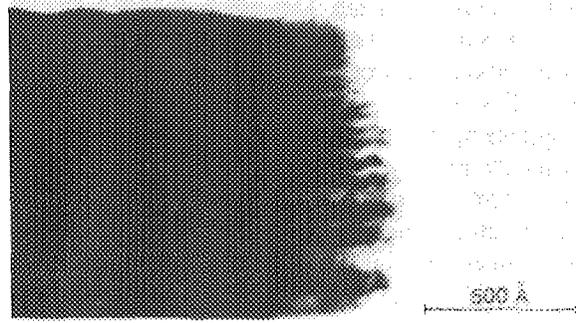


FIG. 5. Transmission electron micrograph of NbN/AlN multilayer detached from substrate with decreasing layer thicknesses from bottom to top.

lattice disorder of a high density-of-states superconductor.<sup>19</sup> For superconducting layer thicknesses less than  $\sim 60$  Å the residual resistivity ratio (RRR, defined as room-temperature resistivity/resistivity at 20 K) decreases rapidly due to increased disorder [Fig. 6(b)]. For instance, a NbN sample made in the same system with a  $T_c$  of 16.1 K had a RRR of 1.21 whereas a typical NbN/AlN multilayer with a NbN layer thickness greater than 100 Å had a RRR of  $\sim 0.8$ . As the NbN layer thickness ( $d_{\text{NbN}}$ ) decreases, parallel critical field slopes at  $T_c$ ,  $[dH/d(1-t)^{1/2}]|_{t=1}$ , where  $t = T/T_c$ , show a definite increase down to a layer thickness  $\sim 60$  Å [Fig. 6(c)]. This increase is in qualitative agreement with the theoretical expectation which predicts a  $1/d_{\text{NbN}}$  dependence. The largest slope occurred for NbN layer thicknesses from 60–70 Å in three series of samples with different AlN layer thicknesses. A rapid decrease of the slopes for  $d_{\text{NbN}}$

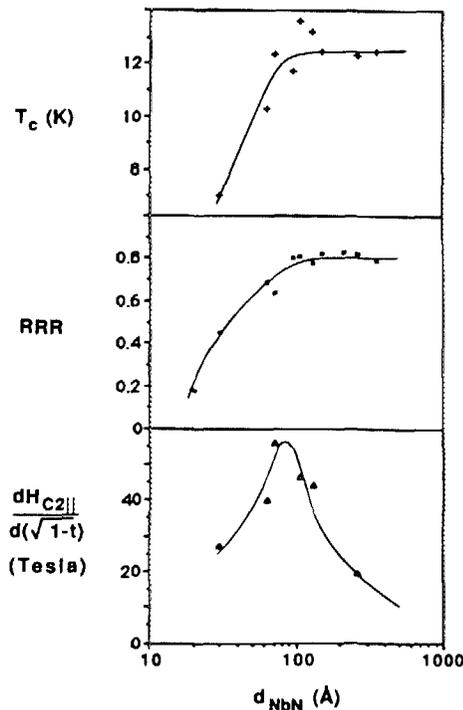


FIG. 6.  $T_c$ , residual resistivity ratio ( $\rho_{293\text{K}}/\rho_{20\text{K}}$ ), and parallel critical field slopes  $\{dH_{c2||}/d[(1-t)^{1/2}]\}$  vs NbN layer thickness for NbN/AlN multilayers with AlN layer thickness of 20 Å.

values less than 60 Å is again attributed to an increase in disorder.

Multilayers with  $d_{\text{NbN}} > 100$  Å have critical temperatures as high as 16 K and low parallel critical field values indicative of "clean," ordered NbN.

## V. CONCLUSION

NbN/AlN multilayers have been fabricated by reactive dc magnetron sputtering by using a proper combination of sputtering gas partial pressures, sputtering rates, and substrate temperature. A preparation procedure for the aluminum target was developed to avoid nitrogen poisoning during deposition. Superconducting critical temperatures, critical field slopes near  $T_c$ , and residual resistivity ratios indicate the introduction of disorder for NbN layer thicknesses less than 60 Å and "clean," ordered NbN for larger NbN layer thicknesses.

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