Coherent epitaxial growth of superconducting NbN ultrathin films on AlN by sputtering

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We investigated the structural and electrical properties of superconducting NbN films epitaxially grown on AlN single-crystalline films using a sputtering technique. The NbN(111) films grown on AlN under optimized temperatures exhibited clear peaks with Pendellösung fringes attributed to the growth of the atomically flat surfaces in 2θ/ω X-ray diffraction patterns. Scanning transmission electron microscopy also confirmed the formation of sharp NbN/AlN interfaces. Reciprocal space mapping revealed that the NbN films were coherently grown on the AlN templates, which indicates that the NbN films have the same in-plane lattice constants as AlN. It was also determined that the shape of the unit cell of NbN depends strongly on the epitaxial growth temperature. The NbN films coherently grown on AlN exhibited superconducting transition temperatures ($T_c$) ranging from 12 to 16 K, which also depends on the epitaxial growth temperature. These results indicate that the epitaxial strain (or change in crystal structure) in NbN modifies $T_c$.

N iobium nitride (NbN) with a superconducting transition temperature ($T_c$) of 15–17 K is a potential material for application in superconductor quantum computers,\(^1\) single photon detectors,\(^2\) and hot electron bolometers.\(^3\) The superconductivity of NbN has been extensively investigated during the past few decades.\(^4\)–\(^6\) Because the properties of NbN are strongly dependent on the crystal structure, lattice constant, and nitrogen content, control of the structural characteristics of NbN films is crucial for realizing quantum devices based on NbN.

Because the (111) planes of α-NbN (NaCl-type) cause relatively small lattice mismatches with group-III nitride semiconductors (−0.2% for AlN and −2.7% for GaN),\(^7\) there is a possibility that a NbN superconductor can be integrated with nitride semiconductors on a single wafer through epitaxial growth.\(^8\)–\(^10\) In fact, N-polar AlGaN/GaN high electron mobility transistors were fabricated on NbN films, which were operated under $T_c$ with a negative differential resistance.\(^11\) The epitaxial integration of nitride semiconductors and superconductors can be applied to the fabrication of Josephson junctions. To realize high-quality all-nitride NbN/AlN/NbN Josephson junctions,\(^12\)–\(^15\) a detailed understanding of the NbN/AlN heterointerfaces is required. However, the epitaxial growth of NbN films on nitride semiconductors has rarely been reported, and little is known about the structural and transport properties of such NbN films.

We have demonstrated the fabrication of light-emitting diodes and high electron mobility transistors based on nitride semiconductors prepared through a sputtering technique.\(^16\)–\(^18\) Although several reports on the deposition of NbN films through sputtering have been published,\(^8\)–\(^10,\)\(^16\) in this study we grew high-quality NbN films using a sophisticated sputtering approach enabling the fabrication of optoelectronic devices. Notably, sputtering is favorable for the deposition of high-melting-point metals such as Nb because it uses electrical energy as a trigger to deliver the source from the target. This differs from molecular-beam epitaxy of NbN where an electron gun must be used instead of an effusion cell. In this study, we investigate the basic properties of ultrathin NbN films grown on single-crystalline AlN films prepared with sapphire substrates through a sophisticated sputtering technique.

Commercially available single-crystalline AlN(0001) (thickness of 1.0 μm)/sapphire templates prepared using metal-organic vapor phase epitaxy (MOVPE) were used as the substrates for the growth of NbN films. The surface of the AlN templates consisted of a step-and-terrace structure, which was derived from the growth of AlN in step-flow mode. The use of atomically flat (0001) planes of AlN is a good choice for the investigation of basic properties of NbN films epitaxially grown on it. The NbN films were grown by applying the proposed sputtering technique. A Nb (99.99% purity) target was sputtered at 60–80 W in an ultra-high-vacuum chamber with a feeding of $N_2$ (99.9999%) gas. After growth, the structural characteristics of the NbN films were investigated using X-ray diffraction (XRD) (Bruker Discover D8 equipped with a one-dimensional detector VÅNTEC-1) and scanning transmission electron microscopy (STEM). The temperature dependence of the resistivity of the NbN films was investigated through a four-probe method using a Physical Parameter Measurement System (Quantum Design). Electron-beam-deposited Au/Ti was used as electrodes for the resistivity measurements.

Figure 1 shows a dark-field STEM image of a NbN/AlN interface grown at 850 °C. The (111) plane of NbN was epitaxially stacked on the (0001) plane of the wurtzite structure AlN. It was difficult to identify the monolayer at the interface because the contrasts and positions of the elements were unclear. From the second layer, the NbN layers were grown in an orderly fashion along the [111] direction. In this field of view, the in-plane epitaxial relationship was determined to be NbN[211][AlN[110]], which reasonably minimizes their lattice mismatch. It is known that AlN(0001) planes possess a strong spontaneous polarization, which will disturb the coherence of superconducting qubits in NbN. For practical use, nonpolar or semipolar plane of AlN is desirable. Even on such planes, the epitaxial relationship between NbN and AlN revealed in this study will be maintained by an appropriate preparation of AlN surfaces before the epitaxial growth of NbN.
Figure 2 shows $2\theta/\omega$ XRD patterns of NbN/AlN structures grown at various temperatures. For example, the sample prepared at 800 °C exhibited clear peaks with Pendellösung fringes attributed to the growth of the atomically flat $\delta$-NbN (111) along with AlN(0001). Interestingly, the shape and peak position of the diffraction from NbN changed as the growth temperature ($T_g$) was increased. First, the peak shifted to a lower angle as $T_g$ was increased from 800 °C to 850 °C. The additional peak then appeared at approximately 35° as $T_g$ increased to 900 °C, which indicates that a phase other than $\delta$-NbN(111) was formed at this temperature. The formation of this additional unidentified phase degraded the crystallinity (coherency) of the NbN, leading to a dissipation of the Pendellösung fringes. An unidentified phase was also observed in the pattern from the sample grown at 980 °C. The NbN again crystallized in a single phase on AlN at 1005 °C, and the peak of the single-crystal NbN shifted to a high angle as $T_g$ increased. Although one possible explanation for the peak shift of $\delta$-NbN(111) to a higher angle was the transformation of a crystal structure into $\beta$-Nb$_2$N(0001), such a phase was not found through an electron back scattered diffraction (EBSD) analysis. These results indicate that the NbN film was compressed along the [111] direction, maintaining a rhombohedral structure rather than a cubic structure. Figure 2(b) shows the $d$-spacing of the 111 diffraction ($d_{111}$) calculated from the peak positions shown in Fig. 1(a). For the NbN film grown at 1200 °C, the value of $d_{222}$ doubled because the peaks for NbN 111 and AlN 0002 were overlapped making the direct calculation of $d_{111}$ difficult. This comprehensive investigation revealed that single-crystal NbN films were grown on AlN except for under temperatures of higher than 850 °C and lower than 1005 °C.

To assess the crystallinity of NbN films, X-ray rocking curves (XRCs) for symmetric 111 and skew-symmetric 004 ($\chi = 54.7^\circ$) diffractions were measured. Analogous to the characterization of wurtzite group-III nitrides, symmetric and skew-symmetric measurements were used for an assessment of the tilt and twist in NbN films. With this concept, AlN 0002 and 1102 correspond to NbN 111 and 004, respectively. Figure 3 shows the full width at half maximum (FWHM) of the XRCs. For comparison, typical FWHM values of XRCs for an AlN template are also displayed. Single-crystal NbN films grown at below 900 °C exhibited an FWHM equal to or slightly larger than those of the template films grown at below 900 °C as $T_g$ was increased to 1005 °C. As $T_g$ was increased to 1200 °C, the tilt (characterized through the measurement of 222 XRC) and twist increased, which indicates that the non-stoichiometry (decrease in N content) of the NbN caused a degradation of the crystallinity. In terms of crystallinity, the optimized growth temperatures could lie within 800 °C and 850 °C or within 1005 °C and 1100 °C. However, as shown in Fig. 2, $d_{111}$ differed (up to 0.5%) between the NbN films grown at 800 °C–850 °C and 1005 °C–1100 °C, which
indicates that their residual strain are completely different. For comparison, we also grew NbN films at 850 °C on AlN templates with higher crystallinity prepared using hydride vapor phase epitaxy. The FWHM values of the 0002 and 1102 XRCs of the high crystallinity AlN template were ∼110 and ∼300 arcsec. The FWHM values of the 111 and 004 XRCs of the NbN film were ∼280 and ∼620 arcsec, which were narrower than those on the AlN templates prepared using MOVPE (shown in Fig. 3). These results indicate that the crystallinity (tilt and twist) of the NbN films were determined based on the crystallinity of the AlN template.

X-ray reciprocal space mapping (RSM) was conducted for a characterization of the lattice constant and crystal structure of NbN films grown on AlN. Figures 4(a)–4(f) show the reciprocal space around AlN 1124. In addition, NbN 240 appeared on the reciprocal plane where AlN 1124 was present because the epitaxial relationship of NbN(111)/AlN(0001) and NbN[211][AlN[100] was satisfied (see Fig. 1). For the samples grown at \( T_g \) ranging from 800 °C to 1030 °C, the inverted in-plane lattice constant \( q_x \) of NbN \((1d_{011})\) coincided with that of AlN, indicating that the NbN films were coherently grown on the AlN templates. The NbN film grown at 1200 °C exhibited an additional reciprocal point attributed to the domain where the lattice was relaxed (labeled as “relaxed”). The \( d_{111} \) value of the relaxed domain was 0.2528 nm, which is approximately the same as \( d_{111} \) of the bulk NbN. The degradation of the crystallinity of the NbN film grown at 1200 °C (see Fig. 3) is due to the lattice relaxation.

The crystal structures of the NbN films were deduced using \( d_{111} \) (out-of-plane) and \( d_{011} \) (in-plane) obtained from the RSMs. Figure 4(g) summarizes the angle \( \alpha \) defined as \( \alpha \) between the sides of the Bravais lattice of the NbN grown at various temperatures. When \( \alpha \) equals 90°, the crystal structure is cubic. In the other cases, the crystal structure is rhombohedral. It was found that the coherently grown NbN films were crystallized in a rhombohedral structure rather than in a cubic structure owing to the strain from the AlN templates. The lattice constant \( a \) of the NbN films also depends on \( T_g \), as shown in Fig. 4(h). The dependence of the crystal structure and lattice constant on \( T_g \) is probably due to the change in the in-plane lattice strain from the AlN and the formation energy of N vacancies. The effect of a deficient N in NbN films on the crystal structure is under investigation.

Figure 5(a) shows the temperature dependence of the resistivity of NbN films grown on AlN at 850 °C, 1030 °C, 1100 °C, and 1200 °C. All films become superconductors at below the critical temperature \( T_c \). Here, \( T_c \) is defined as the temperature where the resistivity becomes half that at 20 K. Figure 5(b) shows the relationship between \( T_c \) and \( T_g \) of the NbN films. The value of \( T_c \) in 27 nm thick NbN grown at 850 °C was 16.0 K, which is relatively higher than that of NbN prepared through different techniques.\(^{16,18}\) Residual
resistivity ratio (the ratio of resistivities at 300 K to 20 K) of this sample was 1.13. In addition, we measured the resistivity ratio (the ratio of resistivities at at 300 K to 20 K) of NbN films grown on AlN at 850 °C, 1030 °C, 1110 °C, and 1200 °C. Although this phenomenon is qualitatively consistent with the results from the literature,6,8) our NbN films exhibited a higher $T_c$ even with the same lattice constant. One of the possible explanations for the dependence of $T_c$ on $T_g$ is a structural transformation from NbN into Nb2N owing to the high $T_g$. However, because we did not observe the formation of $\beta$-NbN by XRD, EBSD, and TEM in this study, the possibility of such a structural transformation can be excluded. It is therefore natural to conclude that the change in $T_c$ stems from the residual stress in NbN constrained by AlN. In summary, we investigated the structural and superconducting properties of NbN films grown epitaxially on AlN through a sputtering technique. It was found that single-crystal NbN(111) films were grown on AlN at temperatures of 800 °C–850 °C and 1005 °C–1100 °C. X-ray RSM revealed that these NbN films were coherently grown on AlN, and the shape of the unit cell was strongly dependent on the growth temperature. Low-temperature resistivity measurements also revealed that the critical temperature of the superconducting NbN films is increased as the lattice constant is elongated. These results can be helpful information for the development of nitride semiconductor/superconductor quantum devices.

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