Epitaxial growth of superconducting NbN on wide-bandgap AlN

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NbN is a superconducting material used in single-photon detectors and quantum bits. Because NbN is lattice-matched to the wide-gap semiconductor AlN, it is possible to integrate the functions of nitride semiconductors and superconductors via epitaxial growth. However, the basic properties of NbN thin films epitaxially grown on nitride semiconductors are still unclear. In this study, we show the structural and electrical properties of NbN thin films grown on AlN by sputtering. We also discuss how the difference in the crystal structure between AlN and NbN leads to the formation of NbN twins.

Received February 22, 2022; Accepted March 16, 2022
Translated from Oyo Buturi 91, 411 (2022) DOI: https://doi.org/10.11470/oubutsu.91.7_411

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1. Introduction

NbN exhibits superconductivity at temperatures of 17 K or lower, and it is used in high-sensitivity photodetection and quantum information processing, such as in single-photon detectors (SPD) [1], hot electron bolometer mixers [2], and superconducting qubits [3,4]. Extensive research has been conducted on NbN, and the first report on its superconductivity dates back to 1941 [5]. The crystal structure of NbN changes in a complex manner depending on the composition ratio between Nb and N, with the most common crystal structure being the cubic rock salt type (6-type, NbN = 1:1). However, crystal structures can take forms such as the hexagonal type (β-type [6,7] and ε-type [8]) and tetragonal type (γ-type) [9] depending on changes in nitrogen composition. The superconducting transition temperature ($T_c$) also changes with the crystal structure, and it is believed that the $\delta$-type, which has a high nitrogen composition, has the highest $T_c$ value. Because a substrate material suitable for the epitaxial growth of NbN thin films has not been developed, research on NbN is centered on bulk crystals and polycrystalline thin films. There are few reports on the structural and electrical characteristics of single-crystal epitaxial thin films.

Interestingly, the (111) plane of $\delta$-type NbN is lattice matched to the (0001) plane of nitride semiconductors, which is used for optoelectronic devices. Among these, the wide-gap semiconductor AlN, regarded as a deep ultraviolet light source [10] and substrate material for high-breakdown-voltage electronic devices [11], has a lattice mismatch with NbN as small as $-0.2\%$.

This implies that an NbN superconducting thin film with low-defect densities can be epitaxially grown on a nitride semiconductor. Several research groups focus on the structural affinity of both materials and have investigated hybrid devices in which NbN superconductors and nitride semiconductors are integrated [3,4,12–15]. However, there are still many unclear aspects regarding the structural and electrical properties of the epitaxially grown NbN thin film. Fabricating new quantum devices using NbN and nitride semiconductors requires an understanding of the basic characteristics of thin films and junction interfaces.

To date, we focused on the development of epitaxial growth technologies for nitride semiconductors using the sputtering method [16,17]. As our sputtering method involves pulsing the raw material with an electric signal as the trigger, the film thickness can be precisely controlled during thin film growth. Furthermore, as high-melting-point metals such as Nb can also be sputtered stably, this is suited for producing NbN ultrathin films. In this study, we first introduce the structural and electrical characteristics of the NbN thin film grown on AlN using the sputtering method [18,19]. Then, we show the mechanism by which twins of NbN grow epitaxially [20]. We also describe the control technology for reducing twin boundaries of NbN [21].

2. Characteristics of NbN epitaxial thin film

Figure 1 shows the X-ray diffraction (XRD) pattern of the NbN thin film grown by changing the substrate temperature from 800°C to 1200°C. For the substrate, we used a commercially-available AlN template prepared on sapphire using the metal-organic chemical vapor deposition (MOCVD) method. The XRD pattern showed a peak derived from the NbN thin film in addition to the AlN 0002 diffraction, and it can be seen that the peak position changes depending on the growth temperature. For example, diffraction from $\delta$-NbN (111) was obtained from the NbN grown at 800–850°C. However, when the growth temperature exceeds 900°C, a new peak appears on the low-angle side of $\delta$-NbN (111). Judging from the diffraction angle and width of the rocking curve, we found that the TiP-type ($\epsilon$-) NbN (1100) was grown at these temperatures. When the

![Fig. 1. XRD 2θ/θ curves of NbN/AlN structures prepared at various temperatures by sputtering [18].](image-url)
growth temperature increased to over 1000 °C, the crystallinity was restored, and diffraction similar to δ-NbN (111) appeared again. A comprehensive analysis that considers film composition revealed by energy-dispersive X-ray spectroscopy, as well as reports from other groups [9], suggests that tetragonal γ-NbN \(_x\) (112) was grown at 1000 °C or higher. Tetragonal NbN\(_x\) has a stoichiometric composition at \(x = 3/4\) [22]. As the XRD peak angle of the series of tetragonal NbN\(_x\) shown here changes continuously with the growth temperature, it is believed that \(x\) slightly deviated from the stoichiometric composition. It is interesting to note that which structure NbN is crystallized is dependent only on the growth temperature.

We conducted X-ray reciprocal space map measurements to reveal the strains in the NbN thin film epitaxially grown on AlN. Figure 2 shows the mapping results around the AlN 1124 reciprocal space. Because the epitaxial relationship of NbN(111)/AlN(0001) and NbN[011] || AlN[1120] is satisfied, AlN 1124 and NbN 240 appear on the same reciprocal space plane. \(q_x\) and \(q_y\) in the map correspond to the reciprocal of the in-plane lattice constant and the reciprocal of the surface normal lattice constant, respectively. \(q_x\) coordinates of NbN and AlN grown at 800 °C and 850 °C match, indicating that the NbN thin films grow coherently on the AlN template at these temperatures. γ-NbN\(_x\) was also coherently grown at 1030 °C. Meanwhile, the reciprocal space map of NbN grown at 1200 °C exhibits a domain with coherent growth as well as multiple reciprocal points, suggesting the occurrence of partial changes in the crystal structure and lattice relaxation. Our recent study has shown that hexagonal \(\beta\)-NbN grows epitaxially on AlN at high temperatures above 1200 °C [23], and the structural transition from the \(\gamma\)-type to \(\beta\)-type is likely observed in this measurement. Coherent growth of NbN on AlN requires precise control of the substrate temperature and setting it within the temperature range where the \(\delta\)-type or \(\gamma\)-type grows (900 °C or less, and around 1050 °C).

Next, we measured the low-temperature resistivity of NbN/AlN prepared at different growth temperatures and investigated the relationship between the crystal structure and \(T_c\) (Figs. 3(a) and 3(b)). The results showed the tendency for \(T_c\) to decrease with increased growth temperature. Wright et al. [9] reported on the relationship between the \(T_c\) of NbN grown on a SiC substrate and the growth temperature of molecular beam epitaxy (MBE). Their study showed that the maximum \(T_c\) of 15.5 K was achieved at a growth temperature of 1000 °C. A different trend was observed in the present study (Fig. 3(b)). It is generally known that the \(T_c\) of a nitride superconductor changes with the impurity concentration and N composition. As the incorporation mechanism of these point defects differs between the sputtering and MBE, there will be differences in the growth temperature dependence of

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![Fig. 2. Reciprocal space maps around AlN1124 diffraction for NbN/AlN structures [18].](image)

![Fig. 3. (a) Resistivity of NbN films at low temperatures. (b) Correlation between the growth temperature and the critical temperature \((T_c)\) of NbN. (c) Correlation between the film thickness and \(T_c\) of NbN. Data for NbN grown by sputtering are from Ref. 18.](image)
Tc Figure 3(c) summarizes the relationship between Tc and film thickness of NbN thin films fabricated using various methods [24–29]. Because these reports differed in the growth conditions and substrate used, the maximum Tc value also differed, but the overall trend was that the Tc increases as the film thickness increases. The Tc of NbN grown on AlN at 850 °C (film thickness of 27 nm) was 16.0 K, and this value could be said to be equal to or higher than that of NbN of the same film thickness fabricated using other methods.

3. NbN twin nanostructures formed on AlN

Thus far, we emphasized the small lattice mismatch between AlN and NbN. However, although AlN (hexagonal wurtzite type) and NbN (cubic rock-salt type) have the same arrangement of N atoms on the topmost surface (triangular lattice arrangement), the periodicity of the entire crystal differs. When a cubic crystal (111) is grown epitaxially on a hexagonal crystal (0001), twins with an in-plane orientation of 60° rotation may be formed. For example, twinning has been confirmed with ScN (111) growth on GaN (0001) [30] or heteropolytype growth of SiC [31]. NbN(111)/AlN(0001) fabricated using sputtering is no exception, and twins have been detected via XRD measurements [32]. Furthermore, twins were also obtained in NbN/6H-SiC grown by MBE [9]. Notably, there is an inherent essential crystal growth mechanism that does not depend on the growth technique. In this section, we clarify the mechanism by which NbN twins are epitaxially grown on AlN.

Figures 4(a)–4(c) show the surface atomic force microscopy (AFM) images of the AlN template and the NbN that is epitaxially grown on it. Steps with a height of 0.25 nm that were generated as a result of step flow growth exist at intervals of approximately 120 nm on the AlN surface (Fig. 4(a)). The NbN grown on this is composed of triangular grains with a width of approximately 20 nm (Fig. 4(b)). Because (111)-oriented NbN is grown, the stable facet {nnl} (where n and l are integers, and n < l) planes are exposed, creating triangular morphology when observed from the surface. This {nnl} plane exhibits a three-fold rotational symmetry with respect to the [111] axis. Careful observation of Fig. 4(c) shows that the direction of the triangular grain of NbN is rotated 180° (60°) with respect to the adjacent terrace.

In other words, it can be inferred that a single crystal with the same crystal orientation grows on the same AlN terrace, but beyond AlN steps, the in-plane orientation of NbN rotates 180° and grows as a twin.

We conducted electron backscatter diffraction (EBSD) measurements to verify the twin crystal formation mechanism inferred from the above AFM observations. Figure 4(d) shows the EBSD in-plane crystal orientation map of NbN. It can be seen that the in-plane crystal orientations are periodically inverted at intervals of approximately 130 nm. Because the period of this twin structure is consistent with the inversion period of the NbN triangle and the step interval of AlN in the AFM images, it can be concluded that the step terrace structure of AlN causes the formation of the NbN twins.

Here, we use Fig. 5(a) to explain an ideal stacking model of a wurtzite-type and rock-salt type structures. In the wurtzite-type AlN (0001), Al–N pairs (bilayers) are stacked in the order of ···ABAB···, and in the rock-salt type NbN (111), the Nb–N bilayers are stacked in the order of ···ABCABC··· or ···CBACB···. Figure 5(b) shows the results of high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) observations of the NbN/AlN interface. Field 1 is a cross-sectional STEM image of the lower terrace of the AlN atomic step, and field 2 is a cross-sectional STEM image of the upper terrace. The stacked sites of A, B, and C are labeled on each bilayer of AlN and NbN. These images were captured in the [1210] direction inclined 30° from the direction in which the AlN atomic step travels (see Fig. 4(a)) such that the adjacent twins can be observed at the same time. Only the Al and Nb atoms are observed as bright spots in this HAADF-STEM image. Incidentally, the position of the N atom is not captured owing to the dynamic range of the annular dark-field detector. A circular bright-field method or differential phase contrast method is needed to simultaneously locate the atomic positions of Nb, Al, and N. When focusing on the interface of field 1, it can be seen that AlN terminates at the B site, and the first layer of NhN grows from the A site. NbN is then stacked in the order of ABCABC··· and crystalized as a rock-salt type structure. In other words, NbN is epitaxially grown such that the stacking order of the first two layers is
the same as the stacking order of the topmost two layers of AlN (AB). In this stacking order, the epitaxial relationship of NbN(111)/AlN[1210] is realized.

Meanwhile, AlN ends at the A site in field 2, which is one step higher. In this case, the duplication of the stacking order occurs, and NbN initiates epitaxial growth with the same stacking as the two outermost layers of AlN (BA), after which this stacks with CBACBA... Due to this stacking order, NbN[011] is parallel to AlN[1210] in field 2, and the epitaxial relationship is inverted 180° with field 1.

As described above, HAADF-STEM observation revealed the interesting mechanism of crystal growth in which the topmost AlN bilayer determines the stacking order of NbN and even inverts the crystal orientation.

4. Enlargement of single crystal NbN grain

If the crystal orientation of NbN on AlN can be aligned with a size in the order of micrometers, then a new device structure may be achieved in which a nitride semiconductor and superconductor are stacked. For example, we can consider the epitaxial integrated structure of NbN-SNSPD and GaN-HEMT amplifier.

As mentioned in the previous section, NbN on AlN has a high density of twin boundaries induced by atomic steps. In other words, single-crystal NbN without twins could be obtained on step-free AlN surfaces. This inference could be assumed to be valid, given that NbN with the same crystal orientation grew on the AlN terrace with a width of approximately 100 nm (Fig. 4). There are reports on an excellent method for the fabrication of step-free GaN using MOCVD, such as selective-area growth on dislocation-free GaN templates [33] and step-flow growth on a mesa-processed region [34]. Meanwhile, a step control method for AlN has not been established. In this section, we introduce a technique for expanding the single-crystal region of a thin NbN film based on the modification of the AlN surface structure via high-temperature annealing [35].

The top row of Fig. 6 shows the surface AFM image of AlN before and after high-temperature annealing treatment. The AlN surface before annealing exhibits a morphology with small mounds. Annealing at 1200 °C and 1600 °C result in surface atom rearrangement and changes in step shape and density. Annealing at 1700 °C promotes step bunching, and flat terraces without steps over a range of 1 μm or more appear.

The bottom row of Fig. 6 shows the surface AFM image of NbN grown on the flattened AlN. It can be seen that the bunched steps are inherited by NbN as well. Due to this stacking order, NbN[011] is parallel to AlN[1210] in field 2, and the epitaxial relationship is inverted 180° with field 1.

As described above, HAADF-STEM observation revealed the interesting mechanism of crystal growth in which the topmost AlN bilayer determines the stacking order of NbN and even inverts the crystal orientation.
height of AlN is an even-numbered bilayer. Please refer to the work by Kihira et al. (Ref. 21) for the model.

5. Conclusion

In this study, we introduced a technique for epitaxially growing a nitride superconductor NbN on AlN. It was found that changing the epitaxial growth temperature enabled control of the NbN crystal structure and superconducting transition temperature. We also clarified the mechanism for the formation of the periodic twin structure that resulted from differences in the crystal structures of AlN and NbN. Furthermore, we introduced a method for expanding the single-crystal region of NbN using the twin crystal formation mechanism. We expect that the epitaxial NbN/AlN will become an interface that connects the functions of the nitride semiconductor and superconductor, which have each been independently developed, and that this contributes to the development of novel quantum devices [13,36].

Acknowledgments

This work was supported by JSPS KAKENHI (Grant No. JP21H01827), the Murata Science Foundation, Iketani Science and Technology Foundation, and Nippon Sheet Glass Foundation for Materials Science and Engineering. We also thank Shunya Kihira of The University of Tokyo for the fabrication and analysis of the samples. The low-temperature resistivity measurements were conducted using the facilities at Cryogenic Research Center, The University of Tokyo.

References

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