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Transition temperatures and upper critical fields of NbN thin films fabricated at room temperature

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Abstract

NbN thin films were deposited on thermally oxidized Si substrate at room temperature by using reactive magnetron sputtering in an Ar-N_2 gas mixture. Total sputtering gas pressure was fixed while varying N_2 flow rate from 1.4 sccm to 2.9 sccm. X-ray diffraction pattern analysis revealed dominant NbN(200) orientation in the low N_2 flow rate but emerging of (111) orientation with diminishing (200) orientation at higher flow rate. The dependences of the superconducting properties on the N_2 gas flow rate were investigated. All the NbN thin films showed a small negative temperature coefficient of resistance with resistivity ratio between 300 K and 20 K in the range from 0.98 to 0.89 as the N_2 flow rate is increased. Transition temperature showed non-monotonic dependence on N_2 flow rate reaching as high as 11.12 K determined by the mid-point temperature of the transition with transition width of 0.3 K. On the other hand, the upper critical field showed roughly linear increase with N_2 flow rate up to 2.7 sccm. The highest upper critical field extrapolated to 0 K was 17.4 T with corresponding coherence length of 4.3 nm. Our results are discussed with the granular nature of NbN thin films.

Keywords: Niobium nitride thin film, reactive magnetron sputtering, granular superconductivity, nitrogen flow rate

1. INTRODUCTION

The fabrication and superconducting properties of NbN films have been extensively studied for more than 40 years [1]. The potential applications are Josephson junctions, single-photon detector, and so on [2]. Higher transition temperature (T_c) of 17 K has been one of the advantages to use NbN in place of Nb. Most NbN films have been deposited by reactive magnetron sputtering in an Ar- N_2 mixture [1-4] but sometimes pulsed laser deposition [5] or atomic layer deposition method [6] was also used.

During the sputtering process, various deposition parameters such as choice of substrates, deposition time, power supplied to the target, substrate temperature, and gas pressure, can affect the film quality. To obtain a high T_c and a low normal-state resistivity, substrates such as single-crystalline MgO [7] and Al_2O_3 [8], which have low lattice mismatch with NbN, have been used for the epitaxial growth. In the case of using Si as substrates, buffer layer of TiN or Al_2O_3 was used to reduce large lattice mismatch between Si and NbN [9]. Our purpose for preparation of NbN thin film is to use it in a spin-switch device as a passive superconducting layer sandwiched between two ferromagnetic layers. In this case, a large mismatch between the ferromagnetic layers and NbN is inevitable. So it is meaningful to fabricate NbN films on lattice mismatched substrates such as thermally oxidized Si.

To obtain high T_c of around 16 K, NbN films were often deposited at elevated temperatures of around 300°C [7-8]. However, in the case of multilayers such as spin-switch devices, multilayers grown at elevated temperatures can be vulnerable to alloying of two different materials at interfaces. This kind of interfacial alloying is known to degrade performance of spin switch devices. In order to reduce adverse alloying effect we selected room temperature deposition despite of scarifying some merits that belong to high quality NbN films. Furthermore, to simplify the deposition condition, the deposition time, the sputtering power, and the total chamber pressure were fixed throughout this work. The only variable of the sputtering is the Ar to N_2 flow ratio which was controlled by changing the N_2 flow rate while Ar flow rate was fixed. In this work, we report the dependence on the N_2 flow rate of the superconducting transition temperature and upper critical field of NbN thin films fabricated at room temperature.

2. EXPERIMENTAL

NbN thin films were deposited on thermally oxidized Si substrate without any additional heating by dc reactive magnetron sputtering of pure Nb target in an Ar- N_2 gas mixture. The base pressure of the system after overnight pumping was lower than 3×10^{-7} Torr. During the deposition, total sputtering gas pressure was fixed at 2.75×10^{-3} Torr while varying N_2-gas partial pressure by adjusting flow rate of N_2 gas from 1.4 to 2.9 standard cubic centimeters per minute (sccm). For the above range of N_2 flow rate, the N_2 partial pressure increased almost 5 times, but its contribution to the final chamber pressure was minimal, in such the total pressure was mainly due to Ar gas pressure. The sputtering power was kept at around 140

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W and the deposition time was fixed for 5 min.

The thicknesses of the films obtained using Alpha Step varied from 185 to 120 nm as N_2 flow rate was increased from 1.4 to 2.9 sccm while showing approximately a linear decrease of growth rate with increasing N_2 flow rate. The film structure was characterized by x-ray diffraction (XRD) through θ-2θ scan using Cu K_α source. The atomic weight percentage ratio was determined by energy dispersive X-ray spectroscopy (EDS). For the transport measurement, Hall-bar shape was fabricated by using a lift-off technique. The temperature dependence of resistivity was measured by using a conventional dc four-probe method in a Physical Property Measurement System up to a maximum field of 9 T applied perpendicular to the substrate.

3. RESULTS AND DISCUSSION

Fig. 1 shows the representative XRD scans for six NbN thin films as a function of 2θ. We focus on two NbN peaks for (200) and (111) orientation at around 41° and 35°, respectively. The other sharp peaks at around 33° are from Si substrate. Broad NbN peaks compared to the sharp Si-substrate peak indicate polycrystalline nature of the films. Using the Scherrer's formula, we estimate the grain size in the range from 3 to 7 nm. For low N_2 flow rate below 2.0 sccm, only (200) orientation is observed. In this flow rate, the nominal N to Nb atomic weight percentage ratio determined by EDS was less than 1 indicating insufficient nitriding of Nb. At around optimum N to Nb ratio of 1, which corresponds to 2.0- and 2.2-sccm samples, (111) orientation emerges and, at the same time, (200) orientation diminishes.

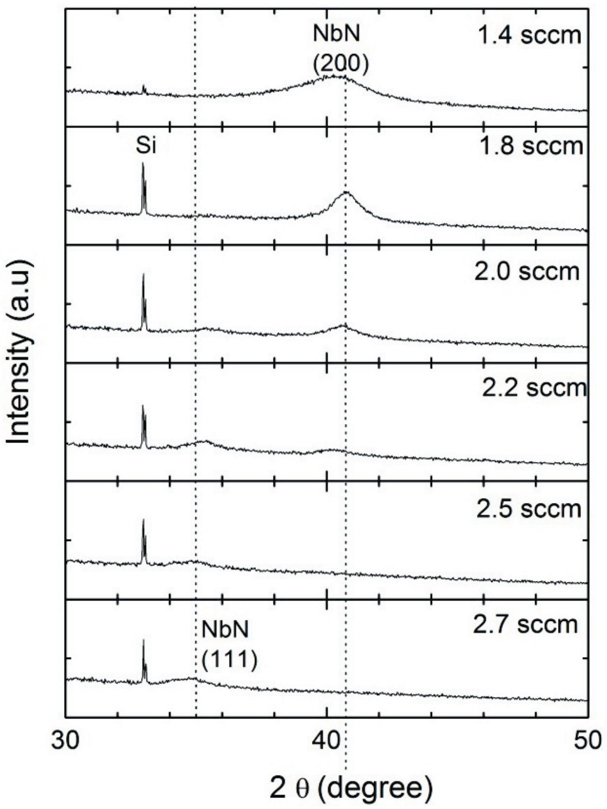

Fig. 1. X-ray diffraction patterns of NbN thin films deposited on thermally oxidized Si substrate at different N_2 flow rates.

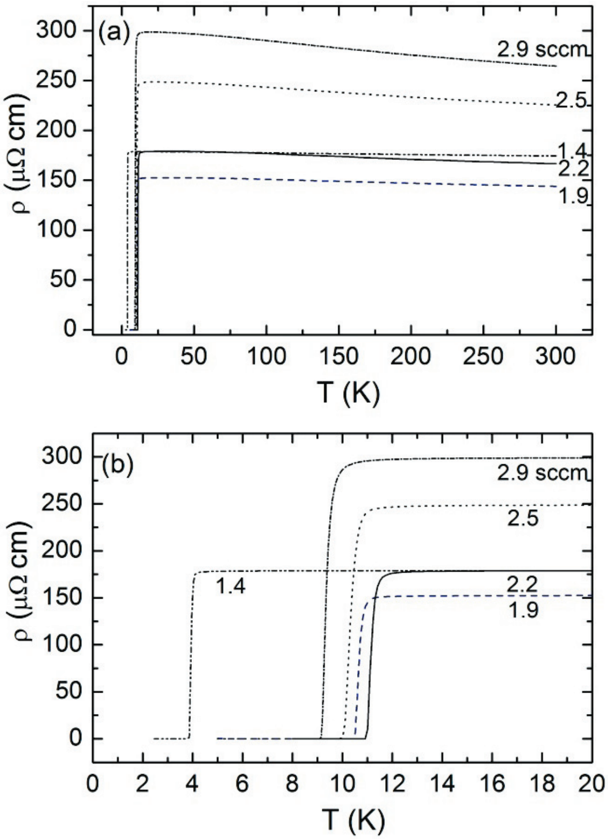

Fig. 2. (a) Resistivity (ρ) vs temperature (T) curves for NbN films deposited at different N_2 flow rates. No magnetic field is applied. (b) Expanded view near the superconducting transition.

Above 2.5 sccm where N to Nb ratio is greater than 1, only (111) orientation is observed. The reason behind the change of growth orientation with N_2 flow rate increase is not exactly known but the present results seem to indicate that the lower growth rate at the higher N_2 flow rate may prefer (111) orientation. The shifts of (200) and (111) peaks with nitrogen content are also observed suggesting that the lattice constant is sensitive to the nitrogen content.

Resistivity (ρ) as a function of temperature for a few representative NbN films in an ambient magnetic field is shown in Fig. 2. The details in the transition region are shown in Fig. 2(b). When cooling from 300 K the normal-state resistivity of all samples slightly increases showing negative temperature coefficient of resistivity. The ratio of room-temperature resistivity to 20 K resistivity, ρ(300K)/ρ(20K), is a good measure of the slope. We find that the resistivity ratio, which is smaller than 1, decreases almost linearly from 0.98 to 0.89 as N_2 flow rate is increased from 1.4 sccm to 2.9 sccm. This kind of temperature dependence is commonly observed in polycrystalline NbN films [1-9] and often interpreted as grain-boundary scattering effect [3, 4].

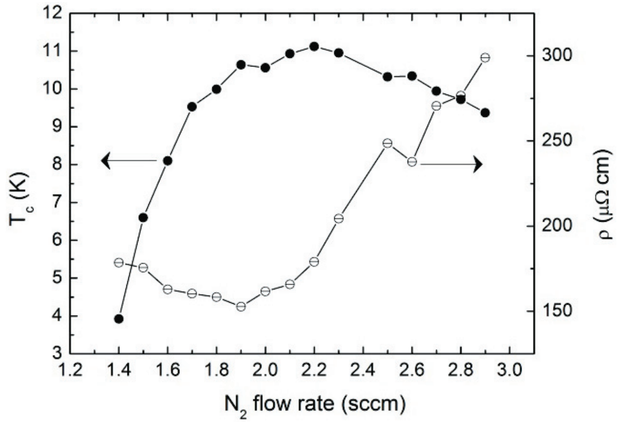

Fig. 3. Transition temperature (T_c) and resistivity (ρ) at 20K are shown for all NbN thin films. Both T_c and ρ exhibit non-monotonic dependence on N_2 flow rate. The highest T_c of 11.12 K was obtained at N_2 flow rate of 2.2 sccm.

T_c and normal state resistivity for all the NbN thin films studied in this work are summarized in Fig. 3 as a function of N_2 flow rate. T_c is defined as the mid-point of the transition. Here one can observe that T_c as well as the normal state resistivity has non-monotonic dependence on the N_2 flow rate.

T_c of NbN films grown between 1.4 and 1.6 sccm are lower than T_c of pure Nb film of 8.7 K grown exactly with same deposition conditions except sputtering gas. In this flow rate range, T_c is more strongly affected by nitrogen content because NbN formation may be far from complete so that there is no connected superconducting path of NbN throughout the samples. The highest T_c of 11.12 K is achieved at 2.2 sccm followed by a decrease with further increase of N_2 flow rate. The transition width defined as the temperature interval between 10% and 90% of the transition was 0.3 K for the film with highest T_c. The largest transition width was 0.6 K observed for the film with 2.8 sccm. Those transition-width values are typically observed in other polycrystalline NbN films [11].

Resistivity decreases slightly as N_2 flow rate increases reaching a broad minimum of 150 μΩcm at around 1.9 sccm before a rapid increase to higher value. So the resistivity, on the other hand, is more strongly dependent on N_2 flow rate at higher rates. In grain-boundary scattering model, the reduction of conductivity depends exponentially on the number of grain boundaries. Then the present results seem to indicate that films get more granular character above 2.1 sccm. However, the reduction of T_c for films deposited with higher N_2 flow rate is not quite strong. It may indicate that lowering T_c and enhancing resistivity may not be due to the same mechanism. That is, grain-boundary scattering is dominant mechanism for normal-state resistivity behavior, but property of the grains themselves is a more important factor in determining T_c.

Fig. 4(a) shows resistive transition of 2.2-sccm NbN film of the highest T_c in perpendicular magnetic fields up to 9 T. Suppression of T_c in an external field can be clearly seen. Fig. 4(b) displays upper critical field (H_{c2}) of the

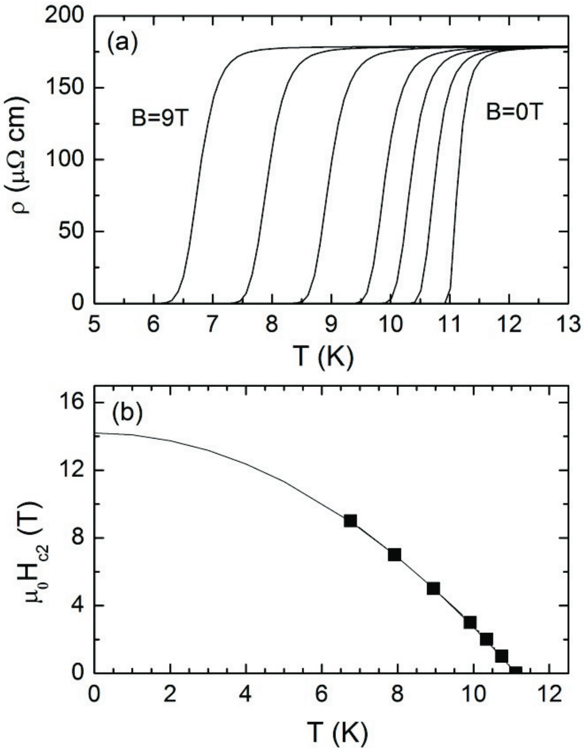

Fig. 4. (a) Resistive transition of 2.2-sccm NbN film in perpendicular magnetic fields up to 9 T. Applied magnetic fields are 0, 1, 2, 3, 5, 7, and 9 T, respectively, from right toward left. (b) Fit of upper critical fields obtained from (a) by applying 50% criterion to the empirical formula for H_{c2} described in (1) in the text.

same film as a function of temperature. Each $\mu_0 H_{c2}(0)$ point in Fig. 4(b) is determined by the field value at which the sample resistivity becomes 50% of the normal state resistivity. Since $\mu_0 H_{c2}(0)$ at 0 K is beyond the capability of our measuring system, we used well-known formula to estimate $\mu_0 H_{c2}(0)$. The solid line in Fig. 4(b) is fit to the empirical equation given by

$$H_{c2}(T) = H_{c2}(0)\left(1-\left(\frac{T}{T_c}\right)^2\right) \quad (1).$$

As can be seen in Fig. 4(b), the experimental results denoted as black squares fit to (1) very well. The obtained $\mu_0 H_{c2}(0)$ are plotted in Fig. 5. Upper critical field increases almost monotonically from 4.7 T with N_2 flow rate of 1.4 sccm to the maximum of 17.4 T for the film grown at N_2 flow rate of 2.7 sccm, followed by a slightly decrease to 16.9 T. These values are in the same range of the published data [10]. The Ginzburg-Landau coherence lengths at 0 K, $\xi_{GL}(0)$, are determined by using the following relation $\mu_0 H_{c2} = \Phi_0/\left(2\pi \xi_{GL}{}^2\right)$ where Φ_0 is the flux quantum. $\xi_{GL}(0)$ decreases from 8.2 nm to 4.3 nm as N_2 flow rate is increased. The corresponding results are also plotted in Fig. 5.

One interesting point is that $\mu_0 H_{c2}(0)$ keeps increasing in the region from 2.2 sccm to 2.7 sccm where T_c starts to decrease. This fact may imply that although excess nitrogen atoms in films degrade the superconducting

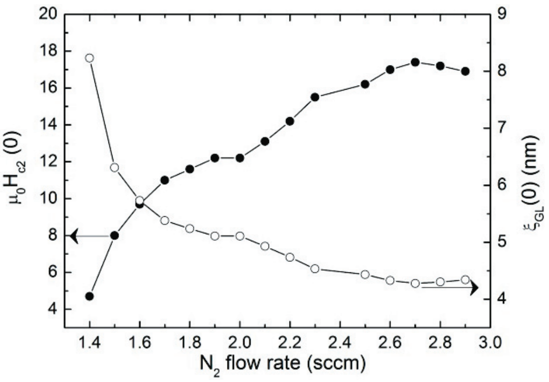

Fig. 5. Dependence on N_2 flow rate of upper critical field and corresponding coherence length at 0 K. It is interesting to note that $\mu_0 H_{c2}(0)$ keeps increasing with flow rate even in the region where T_c starts to decrease.

properties of the grains, they may be beneficial to the pinning properties of the samples. Though exact morphology for the nitrogen-excess films is not known to us, one conjecture would be that some of nitrogen atoms may enter into the grain boundaries and make them to have better pinning characteristics. Of course, too excessive nitrogen content would eventually degrade both the superconducting and pinning properties, which is the case for N_2 flow rate higher than 2.7 sccm. The more detailed analysis for the role of the excess nitrogen would be an interesting future topic.

4. SUMMARY

We have studied superconducting properties of NbN films grown at various N_2 partial pressures. The highest T_c was 11.12 K and the highest $\mu_0 H_{c2}(0)$ was estimated as 17.4 T. Those values were obtained from separate films grown at two different N_2 flow rates, which may imply that dependences on the N_2 flow rate of the transition temperature and upper critical field are somewhat different from each other. In other words, roles of the off-stoichiometric nitrogen atoms in the grains and grain boundaries may be different on the transport properties.

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