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Epitaxial growth of NbN on an ultrathin MgO/semiconductor system

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NbN epitaxial growth on an ultrathin MgO/semiconductor system was carried out by reactive sputtering. It was revealed that (100)-oriented NbN epitaxy was achieved on a (100)-oriented Si substrate by introducing a MgO buffer layer as thin as 5 Å at the interface. An interrupt-sputtering technique was newly conducted to obtain the epitaxial films, which were intermittently deposited by rf sputtering. A metal-insulator-semiconductor tunneling Schottky diode with epitaxial NbN was prepared using this technique, and evaluated in its current-voltage characteristics. Our study indicated that the NbN epitaxy mechanism can be explained by its growth on a (100) naturally oriented 5-Å MgO layer.

I. INTRODUCTION

Superconductor-semiconductor junctions have become of technological importance as new superconducting devices were proposed. Devices such as superconductor-base transistors (SUBSIT),^{1,2} superconductor-base hot-electron transistors (Super-HET),^{3,4} Josephson field-effect transistors,⁵ and so on,⁶ need a clean interface between superconductor and semiconductor since they make use of the electron transport through the junction. Especially in the SUBSIT and Super-HET devices, the intense scattering inside the base layer with the grain boundary and the impurities may reduce the current transfer efficiency. We have pointed out the significance of the epitaxial growth of superconductor on semiconductor for getting ideal hot-electron transport properties in the Super-HETs.^{7,8}

Nb and NbN are promising candidates for device application because they are refractory metals and have high superconducting transition temperatures. Their epitaxial growths on α -Al₂O₃ and MgO have been reported.^{9,10} However, epitaxial growth on semiconductors has several problems, such as lattice mismatching, alloying, and micrograph formation. Therefore, reports on Nb(or NbN)/semiconductor epitaxial growth are still very few. Very recently, Eizenberg *et al.* reported the Nb growth study on GaAs using electron beam deposition.¹¹ They obtained (100)-oriented Nb growth on (100)-oriented GaAs although the Nb/GaAs system has large lattice misfit (~17%). The reaction between Nb and GaAs was avoided because of the slow Nb growth at the substrate temperature of 170 °C. However, the film had a small grain size of less than 20 nm. NbN is a more attractive material than Nb for a high frequency application, because NbN has an onset of pair breaking at a frequency of more than 1500 GHz, whereas this onset occurs in Nb at frequency of about 700 GHz. In order to easily obtain a good superconductivity of the NbN thin film, we have to depend on a reactive sputtering technique. The sputtering deposition on the semiconductor usually produced damage on the surface, resulting in a creation of the alloying and micrograin layers.¹² We have tried the epitaxy on several semiconductors, but have not yet achieved this epitaxy due to the alloying and/or the imperfection of the surface cleaning. The metal-insulator-semiconductor (MIS) structure is an alternative candidate for making a good junction. The ul-

trathin insulator would cause its electrical characteristics to closely correspond to those of a metal semiconductor. NbN is well known to grow epitaxially on (100)-oriented MgO films. Therefore, if we could obtain the (100)-oriented ultrathin MgO film on a semiconductor, the NbN epitaxy on a semiconductor could be realized.

In this work, we study NbN epitaxial growth on semiconductors by introducing an ultrathin MgO buffer layer at the interface. The NbN films were prepared by a new deposition method, interrupt sputtering, in which the film was intermittently deposited to avoid plasma heating damage during film growth. Using this technique, the NbN epitaxy was successfully achieved on Si by inserting MgO as thin as 5 Å between Si and NbN. Characterization of the deposited films was done by x-ray diffraction. As an application for the devices, Schottky diode characteristics with MIS structures were investigated. Furthermore, epitaxial NbN films were obtained on MgO (10 Å)/*n*-Si, which included the selectively doped *p*-type layer. This technique enabled us to construct the device on the plane-patterned substrates.

It should be emphasized that this technique can provide a high-quality material not only for the devices stated above, but also for a number of applications i.e., to an SIS junction, other cryogenic devices, metal-base hot-electron transistors, etc.

II. EXPERIMENTAL PROCEDURE

A. Substrate preparation

Si, GaAs, InP, and GaSb substrates were used for this study. Commercially polished Si and GaAs wafers were etched with HF solutions for 2 min, and InP and GaSb wafers were mechanochemically polished with Br-methanol and boiled in ethanol. All of the wafers were then rinsed in water and dried by N₂, and introduced into the deposition chamber. We could not obtain the mirror surface of the GaSb.

B. MgO deposition conditions

MgO films were deposited by rf sputtering of a 4N pure MgO target in 5N pure Ar gas under a total pressure of 5.6 Pa, a substrate temperature of 300 °C, and a power of 50 W. The deposition rate was 11 Å/min. Prior to the deposition,

the films were baked for 30 min in chamber at a substrate temperature of 300 °C, and presputtered for 30 min. The residual pressure was kept as low as 5.0×10^{-6} Pa.

C. NbN deposition conditions

The NbN film formation was carried out by rf reactive sputtering of a 4N pure niobium target with a 5N pure mixture of Ar and 3.5% N₂. The superconducting transition temperature T_c of the films deposited onto glass substrates strongly depends on the sputtering conditions, such as sputtering power P_s , substrate temperature T_{sub} , and total pressure P_T . To get a high transition temperature, a high T_{sub} , a large P_s , and an optimized P_T were required. However, we have to choose the condition which causes the least damage to the thin MgO on the semiconductor. We chose a P_T of 3.5 Pa, P_s of 50 W, and T_{sub} of 200 °C, leading to a deposition rate of 30 Å/min. Prior to the deposition, the sputter cleaning on the MgO surface was done at a P_s of 5 W for 2.5 min. The film thickness of the NbN was kept to 900 Å thick. The 900-Å-thick NbN film routinely had a superconducting transition temperature of 14.5 K.

In addition, the new sputtering method was introduced to avoid surface damage during deposition. Since continuous sputtering deposition causes sample heating which would create the alloying layer and the micrograin, the NbN films were intermittently deposited by the interrupt-sputtering technique. The process is the following: a shutter is opened for 3 min and closed for 3 min, after which the same procedure is periodically repeated. This technique drastically improved the film crystal quality as discussed in a later section.

D. Characterization of the epitaxial films

The films were characterized by an x-ray diffraction study and electrical measurement of the MIS tunneling Schottky diode curves. The epitaxial ratio of the NbN films were determined by the factor of $I_{200}/(I_{200} + I_{111})$, where I_{111} and I_{200} are, respectively, the intensity of the x-ray diffraction pattern of the (111) and (100) orientations of the NbN films.

III. RESULTS AND DISCUSSION

A. MgO deposition on semiconductors

MgO epitaxial growth on a semiconductor would become necessary in order to obtain (100)-oriented ultrathin MgO film, since the tunneling device requires that the MgO

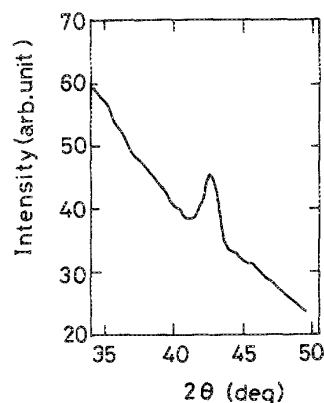


FIG. 1. X-ray diffraction patterns of 600-Å-thick MgO on the Si substrate.

be as thin as its monolayer. Table I gives the lattice constant a of several semiconductors and factor a/a_{MgO} , where a_{MgO} is the MgO lattice constant of 4.21 Å, showing that the factor a/a_{MgO} for the MgO/InP system is almost $\sqrt{2}$. It means that the 45° rotated (100)MgO/(100)InP system has the minimum lattice mismatching of 1.4%. However, even this combination involves a significant lattice misfit, because the B1 structure (MgO) has about twice as many atomic sites than as a zincblende structure.

Apart from the epitaxy, MgO is known to grow with strong preferential (100) orientation regardless of the substrate selection. If this characteristic feature maintains at one monolayer of MgO deposition, it will serve as a good candidate to be the substrate for the overgrowth of the epitaxial NbN.

Figure 1 shows the x-ray diffraction pattern of 600-Å-thick MgO film deposited on the Si substrate. The spectral peak at $2\theta \approx 43^\circ$ corresponds to the (200) diffraction of the (100)-oriented MgO film, which is the same result reported in Ref. 10. The pattern, however, shows a wide shape and small intensity, indicating that the prepared MgO film had a slightly poor crystalline quality. A problem lies in determining the orientation of the quite thin MgO film, for which the diffraction intensity is commonly so weak that the direct observation of the x-ray diffraction becomes useless. Instead, the x-ray analysis made on the overgrown NbN will serve as the diagnosis of the underlying thin MgO film.

The surface morphology of the 30-Å-thick MgO on InP strongly depended on the sputtering condition, whereas mirror surfaces of the MgO on Si, GaAs, and GaSb were easily obtained. Figures 2(a)–2(c) show the micrographs of the MgO surfaces deposited 30 Å on InP at substrate temperatures of 300, 200, and 100 °C, respectively. The substrate temperature strongly affected the surface morphology. Reducing the T_{sub} , the mirror surface was obtained. However, the surface of the 400-Å-thick MgO deposited under the same conditions as in Fig. 2(c) again had a number of spotty defects which were 2–4 μm in diameter. The results suggested that even MgO would easily react with InP due to the sample heating during the sputtering. To avoid the sample heating, we introduced the interrupt-sputtering technique. Using this technique, we prepared the 400-Å-thick MgO films on InP. The surface of the film thus made had a mirror

TABLE I. Lattice constants of several semiconductors.

Semiconductor	Structure	Lattice constant (Å)	a/a_{MgO}
GaAs	zincblende	5.65	1.342
InP	zincblende	5.869	1.394
Si	diamond	5.431	1.290
InSb	zincblende	6.479	1.539
GaSb	zincblende	6.095	1.447
InAs	zincblende	6.058	1.439
CdTe	zincblende	6.477	1.538

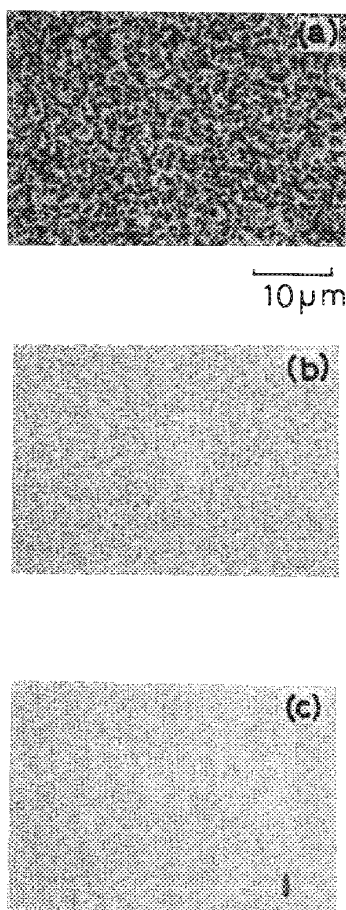


FIG. 2. Photomicrographs of surface morphology of the 30-Å-thick MgO deposited at (a) 300 °C, (b) 200 °C, and (c) 100 °C on InP substrates.

surface. Apparently, this technique is useful for lessening the surface damage for this case as well as for the NbN deposition case. However, we could not determine whether or not the reaction was completely avoided.

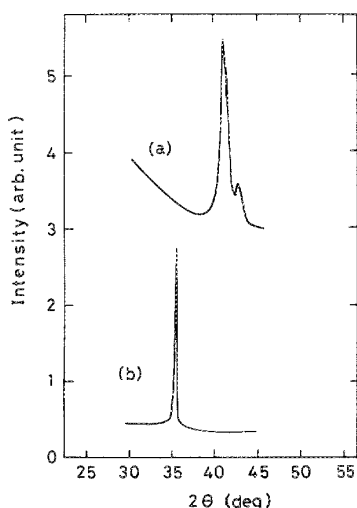


FIG. 3. X-ray diffraction patterns of (a) epitaxial NbN and (b) naturally oriented NbN.

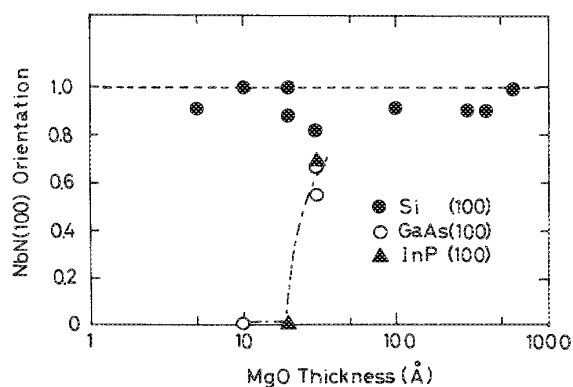


FIG. 4. The NbN epitaxial ratio as a function of the inserted MgO thickness.

B. NbN deposition on an ultrathin MgO/semiconductor structure

1. Epitaxial growth of NbN

NbN is well known to grow epitaxially on (100)-oriented MgO with a lattice mismatch of 4.1%. Figure 3(a) shows the x-ray diffraction curves of 900-Å NbN on 600-Å-thick MgO/Si, revealing that it has a diffraction peak at $2\theta \approx 41^\circ$. This peak corresponds to the (100) texture of the NbN with a $B1$ structure, and it can be compared with the nonepitaxial spectrum shown by curve (b). Namely, the epitaxy of the NbN films was achieved on relatively thick MgO films although the spectra had a wider shape due to the low quality of the MgO film. Our interest was in the NbN epitaxial growth on the ultrathin MgO film. Figure 4 shows the epitaxial ratio as a function of the inserted MgO film thickness. A glance at this figure reveals that by using the Si substrate, the NbN epitaxy was kept as thin as 5-Å MgO, which is almost equivalent to the monolayer. It should be emphasized that the 5-Å-thick MgO is thin enough for the Schottky barriers to work as almost ideal metal semiconductor junctions. On the other hand, using the InP and GaAs substrates, the NbN epitaxy was not achieved on MgO film less than 30 Å thick. This behavior is probably caused by the reaction

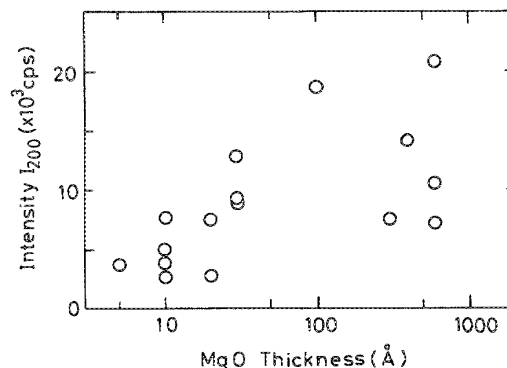


FIG. 5. (200) diffraction peak intensity of the NbN as a function of the inserted MgO thickness.

between MgO and GaAs or InP, which was suggested before by the study of MgO deposition on InP.

Although we achieved the NbN epitaxy on 5-Å MgO/Si, there is a problem with the quality of the epitaxial layer. Figure 5 shows the (200) diffraction peak intensity of the NbN films possessing an epitaxial ratio of almost unity as a function of the inserted MgO layer thickness. As the thickness of the MgO films decreased, the intensity became weak. This suggests that the thin MgO film has low quality and, to get the stable NbN film quality, an MgO film of more than 100 Å is necessary. To get excellent crystallinity of NbN, the MgO layer must be improved in quality by changing the deposition condition or preparation techniques such as electron beam deposition, MOCVD, etc.

An amazing result of this technique is that the NbN epitaxy is achieved on 5-Å MgO/Si even though the MgO/Si structure has a large lattice mismatch (8.8%). Since the mechanism of the (100)-oriented NbN growth originates in the epitaxial growth on the (100)-oriented MgO, it appears that even 5-Å-thick MgO became fully oriented in the (100) direction. To study the mechanism of the MgO growth with the (100) orientation, we carried out the NbN growth on the MgO thermally oxidized Si substrate, where the Si substrate was oxidized in O₂ atmosphere at 1000 °C for 1 h. The NbN epitaxial layer was then obtained even on a 10-Å MgO/SiO₂ structure, which suggests that the mechanism of the epitaxy cannot be explained by the epitaxial growth of MgO but rather by the natural orientation or the graphoepitaxy of MgO. The possibility of a MgO graphoepitaxy might be due to the structural surface deformation introduced during the sputter cleaning of the substrate surface.

On the other hand, as shown in Fig. 2, the alloying between MgO and substrate materials (InP, GaAs) prevented the thin MgO layer from growing with a fully aligned crystal axis. This implies that even natural orientation requires a clear interface free from constituent atom mixing.

2. Interrupt-sputtering technique

The interrupt-sputtering technique improved the film quality. The comparison of this technique and usual sputtering are given in Fig. 6. It reveals that the (200) diffraction peak of the 900-Å-thick NbN film produced by the interrupt-sputtering [Fig. 6(a)] had a larger intensity and a smaller full width at half maximum (FWHM) of the rocking curves than the film prepared by usual sputtering [Fig. 6(b)]. Figure 7 gives FWHM as a function of the inserted MgO layer thickness. A glance at this figure reveals that the new technique provided films with smaller FWHM, shown by open circles, than the continuous sputtering technique, shown by filled circles, regardless of the MgO thickness. Furthermore, the NbN epitaxial layer was not obtained on MgO less than 30 Å thick using the usual technique. The results indicate that the continuous plasma heating of the substrate surface worsened the film crystal quality.

3. Sputter cleaning study

The effect of the sputter cleaning of the substrate surface taken just before the MgO deposition was studied. The *in situ* cleaning was done by Ar ambient (5.6 Pa) with several dis-

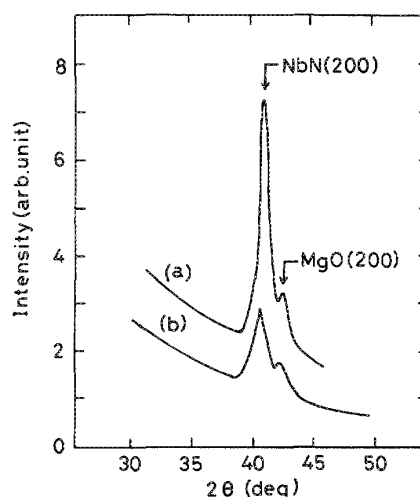


FIG. 6. X-ray diffraction patterns for the films prepared by (a) interrupt sputtering and (b) usual sputtering.

charging powers for 1.5 min. The surfaces of the substrate wafers were usually contaminated with water vapor, hydrocarbon, oxide, etc. To obtain good crystallinity of the NbN/MgO heterolayer, those contaminations had to be eliminated just prior to the film deposition. Figure 8 shows the NbN epitaxial ratio versus sputter cleaning power. The NbN epitaxy on the 10-Å MgO/Si structure does not depend much on the sputter cleaning condition, whereas the epitaxy on the 30-Å MgO/GaAs structure strongly depends on it. At the region of the excess sputtering power, the cleaning process may cause unfavorable surface damage, especially for the GaAs. The optimized power for GaAs was 15 W. However, this cleaning technique would, in principle, simultaneously cause damage of the GaAs, which may become one of the factors that prevents the NbN epitaxial growth on the GaAs substrate. Therefore, the other cleaning techniques such as the thermal removal of the oxide layer, H₂ plasma cleaning, etc. which gives the least damage, must be introduced.

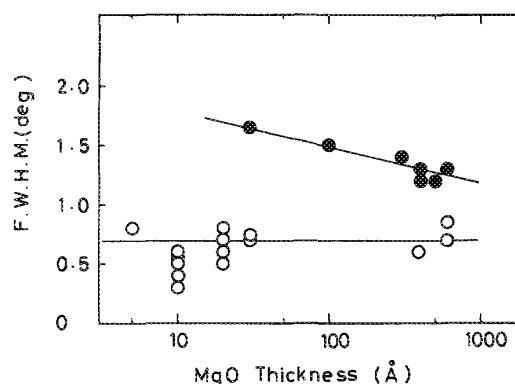


FIG. 7. Full width at half maximum (FWHM) of the rocking curves vs the inserted MgO thickness. Open circles are for the film prepared by interrupt sputtering; filled circles are for those prepared by the usual sputtering.

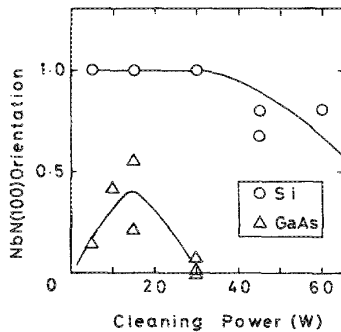


FIG. 8. NbN epitaxial ratio vs sputter-cleaning power. Open circles are for NbN/MgO (10 Å)/Si; open triangles are for NbN/MgO (30 Å)/GaAs.

C. Application for the MIS tunneling diode

1. MIS tunneling Schottky characteristics

The epitaxial NbN/MgO/Si MIS Schottky diodes were fabricated from wafers prepared for this work. The NbN electrodes 100 μm in diameter were made by the conventional photolithography and CF_4 dry etching. MIS tunneling Schottky diode curves measured at room temperature are given in Fig. 9 as a parameter of the MgO film thickness. The dashed curves for the samples with 10-, 20-, and 30-Å-thick MgO were calculated in Ref. 13 by the following formula for the MIS tunneling Schottky diode:

$$I = SA^*T^2 \exp(-a_T \phi^{1/2} d) \times \exp(-q\phi_B/kT) [\exp(qV/kT) - 1],$$

where S is the junction area, A^* is the effective Richardson constant, T is the ambient temperature, a_T is 1.025, $q\phi_T$ is the effective barrier height of the insulator, d is the thickness of the insulator, $q\phi_B$ is the Schottky barrier height, and k is the Boltzmann constant. Except for the term $\exp(-a_T \phi^{1/2} d)$, this is the same expression as that for the thermionic-emission equation for the Schottky barriers. We assumed MgO thicknesses of 8, 18, and 28 Å, respectively, because the MgO could be slightly removed (2 Å) by the sputter cleaning before the NbN depositions. We also assumed a Schottky barrier height for NbN and Si junctions of 0.6 eV and an average MgO effective barrier height of 2.8 eV.¹⁴ The approximate agreement obtained between the experimental and calculated results is shown in Fig. 9.

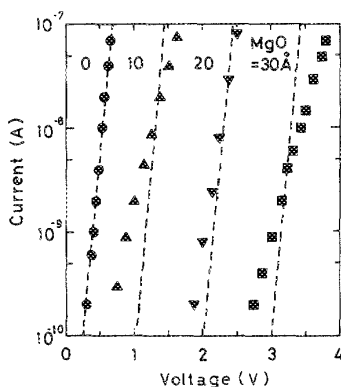


FIG. 9. Current-voltage curves of the prepared MIS tunneling Schottky diode as a parameter of the MgO thickness.

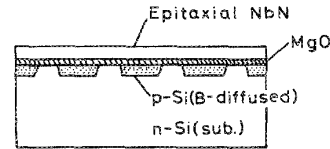


FIG. 10. Schematic drawing of the prepared structure. NbN epitaxy was obtained using n -type Si including a patterned p -type layer.

2. Epitaxial growth on patterned Si substrates

For the device application, a fabrication of the device in a planar structure is important, since a device which is not flat is likely to result in a grain boundary, pin holes, and other defects. We tried NbN epitaxial growth on 10-Å-thick MgO using n -type Si in the patterned p -type layer as drawn in Fig. 10. The p -type layer was patterned by selective boron diffusion into the n -type substrate. The 10-Å MgO film was deposited on the substrate, followed by the NbN deposition in the same manner as described previously. The epitaxial ratio of unity was also successfully obtained even on this substrate wafer.

IV. CONCLUSION

The most important conclusion of this work is the achievement of NbN epitaxy on the Si substrate by introducing the monolayer MgO buffer layer at the interface. The 5-Å-thick MgO is thin enough to provide the various devices which requires the ideal metal-semiconductor junction. Moreover, it goes without saying that this technique would improve the characteristics and reproducibility of the superconductor-base hot-electron transistor. Other conclusions include the following: The interrupt-sputtering technique was newly introduced in the NbN deposition process, resulting in a large improvement of the crystal quality of the epitaxial NbN film. The NbN epitaxy was achieved on the thin MgO/selectively patterned Si structure, which can provide the device with flat patterning. Good MIS tunneling Schottky characteristics were also obtained.

ACKNOWLEDGMENTS

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