High Field Properties of Nb_3Ge and NbN Films (Low-T_c Superconducting Materials Research)

著者	Suzuki Mitsumasa, Anayama Takeshi
journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	37
number	1/2
page range	35-43
year	1992-11
URL	http://hdl.handle.net/10097/28390

High Field Properties of Nb_3Ge and NbN Films

Mitsumasa Suzuki[a] and Takeshi Anayama[b]
[a]Department of Electrical Engineering, Faculty of Engineering, Tohoku University, Sendai
[b]Hachinohe National College of Technology, Hachinohe
(Received August 6, 1992)

Synopsis

Sputtered and CVD-prepared films of A15-type Nb_3Ge and sputtered films of B1-type NbN have been studied on their high field properties. Further, strain effects of critical current density J_c have been investigated on NbN. The J_c of sputtered Nb_3Ge films exceeds 1×10^5 A/cm^2 at fields up to 20 T. In CVD-prepared films, the J_c is somewhat lower in fields higher than 20 T and is highly affected by their deposition temperature. The upper critical field B_{c2} of two kinds of films is roughly proportional to their transition temperature T_c. NbN films have anisotropy in B_{c2}, which yields strong anisotropy in J_c with respect to the field orientation. The values of J_c are higher in the perpendicular field to a film plane and reach 1×10^5 A/cm^2 at 21 T. The B_{c2} increases with ρ_n. Little change in J_c has been observed under strains above 1 % at 9 T for NbN films on Hastelloy B tape.

I. Introduction

The development of advanced superconductors carrying large currents in magnetic fields higher than 20 T is very important for the realization of high-field magnets. The use of commercially available superconductors such as Nb_3Sn and V_3Ga for high field applications is probably limited to a field range below 18 T at most. Emerging superconductors with high B_{c2}, Nb_3Ge,[1,2] $Nb_3(Al,Ge)$[3], $PbMo_6S_8$,[4] etc., are expected to have critical current densities of practical utility even in fields higher than 20 T. Recently, sputtered films of NbN[5] were pointed out to show very high B_{c2} and very strong tolerance against irradiation[6] and strain.[7] NbN may be also one of the most promising materials for large-scale magnets.

In this report, we present critical current densities J_c at high magnetic fields and upper critical fields B_{c2} in Nb_3Ge and NbN films together with their preparation conditions.

II. A15-type Nb_3Ge

Nb_3Ge films were prepared on sapphire substrates by dc sputtering and chemical vapor deposition(CVD). In the case of sputtering, a single target technique was adopted[8]. Targets were made by arc casting the elements in various ratios and the effects of target composition on the growth of A15 phase were investigated. On the other hand, for the preparation of CVD-films, $NbCl_5$ powder and liquid $GeCl_4$ were used as starting materials. The chloride vapor was mixed with H_2 gas, and then reduced for 30 minutes in a quartz reactor held at a deposition temperature T_d between 750°C and 900°C. The details of the preparation technique have been reported previously.[9]

Some important characteristics of typical Nb_3Ge films are listed in Tables 1 and 2. Here, $T_{c,end}$ indicates zero resistance transition temperature. Most of films prepared by the sputtering normally exhibit T_c exceeding 20 K in resistive measurements. According to X-ray diffraction analysis, a single A15 phase was identified for films deposited from a stoichiometry target, Nb/Ge ratio=3.0. With decreasing the Nb/Ge ratio of targets, an increase in the amount of the second phase(hexagonal Nb_5Ge_3) is observed. From SEM observation, so-called columnar grain structure was found out in these films.[10] As a consequence of a number of sputtering runs using targets with different compositions, high-T_c films of good quality were reproducibly obtained from a slightly Ge-richer target, Nb/Ge ratio=2.8. On the other hand, the T_c of CVD-prepared Nb_3Ge films is somewhat lower. Their microstructure is considerably influenced by the deposition temperature T_d. The size of A15 grains appreciably increases, as T_d is increased from 800 to 900°C. Coarse grains of 1 μm are frequently seen in films deposited at 900°C. From composition

Table 1 Characteristics of sputtered Nb_3Ge films.

Sample number	Thickness (nm)	$T_{c,end}$ (K)	Target Nb/Ge
603	380	21.1	3.0
42	240	21.1	2.8
292	410	20.6	2.6

Table 2 Characteristics of CVD-Nb_3Ge films.

Sample number	Thickness (μm)	$T_{c,end}$ (K)	T_d (°C)
2106	1.78	18.9	800
0703	3.39	20.3	850
0503	4.44	20.7	900

analysis by an electron probe microanalyser, it has been found out that high-T_c films have Nb/Ge ratios of about 2.5 considerably lower than the stoichiometric composition and normally contain a small amount of the second phase.[11)]

Figure 1 shows J_c of three sputtered films measured in the perpendicular field $B\perp$ and the parallel field $B\parallel$ to the film plane. The best film, sample 42, exhibits high J_c exceeding 1×10^5 A/cm^2 up to 21 T and still possesses a J_c value of about 1×10^4 A/cm^2 even at 30 T. There is a slight difference between dependences of J_c on $B\perp$ and $B\parallel$. Especially, in the field region 10-23 T the J_c for $B\parallel$ is somewhat higher. Sample 603 deposited from a stoichiometry target shows similar field dependences of J_c. In sample 292 from a Ge-rich target, its T_c is slightly lowered and an appreciable decrease in J_c is seen in the entire field range.

The results of CVD-prepared films is given in Fig.2. Sample 2106 deposited at low T_d, 800°C, exhibits high J_c in every fields, though its T_c is somewhat lower than those of other films. With increasing the applied field up to 23 T, the film exhibits a monotonous decrease in J_c. Both dependences of J_c on $B\perp$ and $B\parallel$ are very similar to each other. In the case of sample 0703 prepared at T_d=850°C, the J_c is somewhat lower, while its T_c is improved. With further increasing T_d up to 900°C, a marked decrease in J_c is seen in a wide field range for $B\perp$. The difference between dependences of J_c on $B\perp$ and $B\parallel$ enlarges. In particular, the J_c in $B\parallel$ is unchanged in the low field region 5-15 T and is rather high, compared to that for $B\perp$ in fields

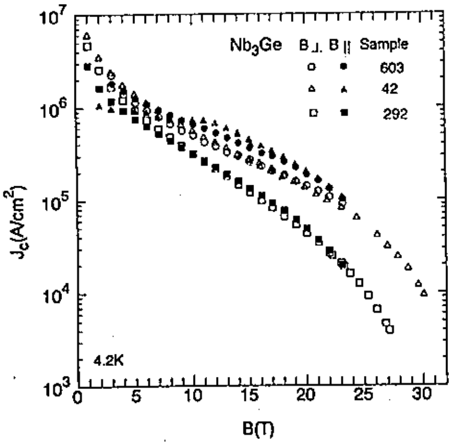

Fig.1 Critical current density of sputtered Nb_3Ge films as a function of applied field.

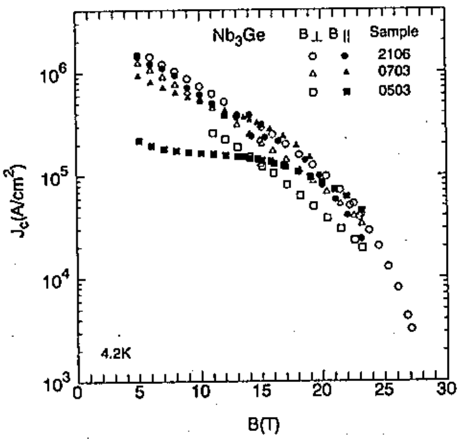

Fig.2 Critical current density of CVD-prepared Nb_3Ge films as a function of applied field.

higher than 15 T. As shown in Figs.1 and 2, the J_c of the best CVD-prepared film is almost the same as that of sputtered films in fields lower than 20 T. A marked difference of J_c between sputtered and CVD-prepared films takes place in fields higher than 20 T. This might be attributable to the difference in B_{c2}.

Figure 3 shows the J_c results of sputtered sample 42 at various temperatures higher than 4.2 K in B⊥ . As seen in Fig.1, the value of J_c at 21 T reaches $1\times10^5 A/cm^2$ at 4.2 K. As the temperature is increased beyond 16 K, the J_c decreases to one tenth or below that at 4.2 K. The B_{c2} values estimated from the Kramer plot are about 34 T at 4.2 K and 11.8 T at 16 K, respectively.

Figure 4 shows B_{c2} of a lot of films at 4.2 K as a function of T_c . The measurements of B_{c2} were carried out in a pulsed field parallel to the flow direction of transport current.[12] As seen in Fig.4, there is a roughly steady increase of B_{c2} with T_c. Especially, sputtered films show a linear increase of B_{c2} with their T_c . The highest B_{c2} of 33.3 T is obtained in sample 42, which is in good agreement with 34 T estimated from the Kramer plot. On the other hand, data of CVD-prepared films are pretty scattered. As compared to the sputtered films, the CVD-prepared films tend to contain crystal phases besides A15 phase. The uniformity of the films is decidedly inferior with respect to thickness and composition. The scatter of B_{c2} for CVD-prepared films is presumably ascribed to their nonuniformity . From

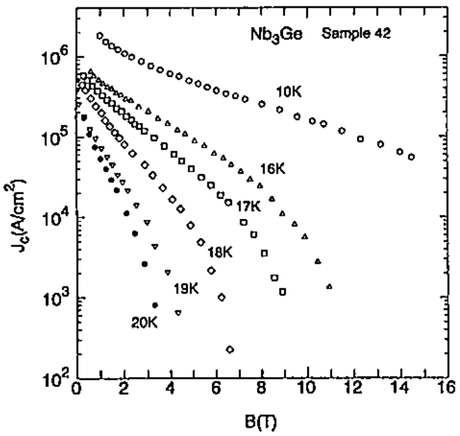

Fig.3 Critical current density of a sputtered film at temperatures higher than 4.2 K as a function of perpendicular field.

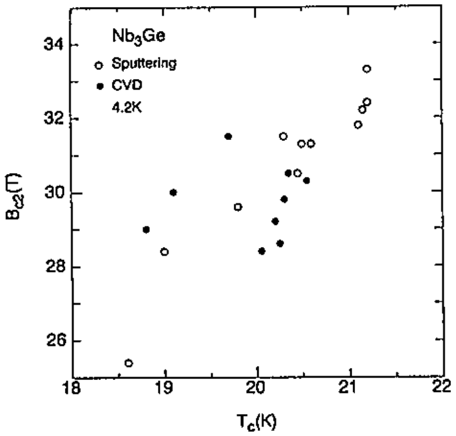

Fig.4 Upper critical field of sputtered and CVD-prepared Nb_3Ge films at 4.2 K as a function of transition temperature.

the obtained relationship between T_c and B_{c2}, the B_{c2} value of the best Nb_3Ge film with a T_c of 23 K is expected to approach 37 T consistent with that for a sputtered film obtained by Foner et al..[13]

III. B1-type NbN

NbN films were prepared on substrates of quartz and sapphire from a Nb disk target in an argon-nitrogen atmosphere by rf sputtering. Substrates were heated to temperatures between 400°C and 700°C. Both argon and nitrogen partial pressures are varied independently. The details of the preparation technique have been reported previously.[14]

The T_c of films is strongly influenced by one of the deposition parameters, nitrogen partial pressure P_{N2}. With increasing P_{N2} from 1 mTorr, the T_c rapidly increases. The maximum T_c value exceeding 16 K is obtained around P_{N2}=4 mTorr. A further increase in P_{N2} provides a slight decrease in T_c and causes an appreciable increase in normal state resistivity ρ_n. Most films deposited at P_{N2} higher than 4 mTorr are identified as B1 phase from X-ray diffraction analysis. According to SEM observation, fine columnar grains of 20-50 nm or less in diameter with the (111) plane parallel to the film surface are seen in films on quartz. Films on sapphire contain an initial growth layer 150 nm thick, on which coarse columnar grains are subsequently formed.[15]

NbN films prepared by sputtering exhibit anisotropy in B_{c2}. Figure

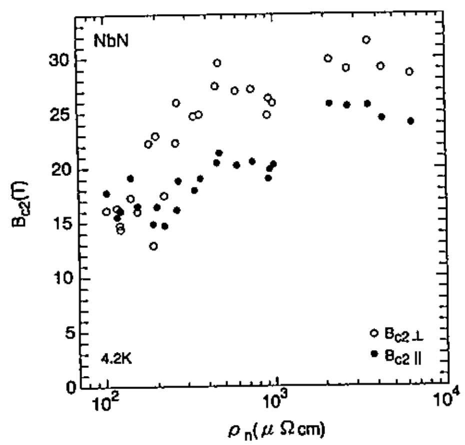

Fig.5 Upper critical field of NbN films at 4.2 K as a function of normal state resistivity.

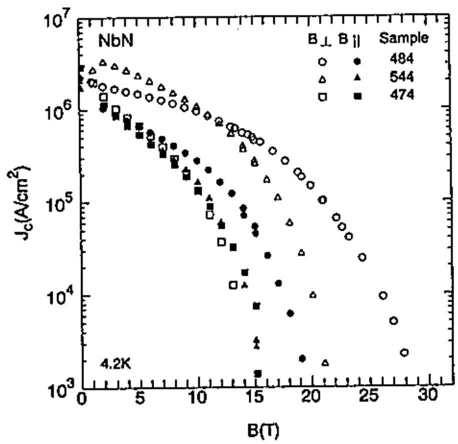

Fig.6 Critical current density of NbN films at 4.2 K as a function of applied field.

5 shows the variations of $B_{c2}\perp$ and $B_{c2}\|$ as a function of ρ_n for all the films on quartz . As can be seen in this figure, Values of $B_{c2}\perp$ and $B_{c2}\|$ are about the same for films with low ρ_n. With increasing ρ_n to 500 μΩcm, the B_{c2} rapidly increases and the anisotropy in B_{c2} appears. There is a small increase in both $B_{c2}\perp$ and $B_{c2}\|$ in the ρ_n range of above 500 μΩ cm. The T_c of high-B_{c2} films falls in the range of 14-15 K. The maximum values of $B_{c2}\perp$ and $B_{c2}\|$ are 30 and 25 T, respectively.

Table 3 Characteristics of sputtered NbN films.

Sample number	Thickness (nm)	T_c (K)	n (μΩcm)
484	280	15.7	470
544	260	16.7	180
474	310	15.8	120

Figure 6 shows J_c results of typical NbN films deposited on quartz. Their important characteristics are listed in Table 3. As can be expected from the results of B_{c2}, dependences of J_c on $B\perp$ and $B\|$ are very different for films with high ρ_n , and higher J_c values are obtained in $B\perp$. The best film, sample 484, has J_c values higher than 1×10^5 A/cm^2 at fields up to 21 T in $B\perp$. As the applied field is further increased from 21 T, the J_c in $B\perp$ rapidly decreases. On the other hand, in $B\|$ higher J_c values than 1×10^5 A/cm^2 are obtained in a field range below 15 T. In spite of this large anisotropy in J_c, it should be noted that the J_c in the $B\perp$ range of 5-20 T is higher than that for Nb_3Ge films. Data of J_c at 15 T are given as a function of ρ_n in Fig.7. Dependences of J_c in $B\perp$ and $B\|$ on ρ_n are clearly different. Namely, the J_c in $B\perp$ is higher in the entire ρ_n range and gradually decreases with ρ_n. In $B\|$, the J_c shows maximum around 1000 μΩcm where a J_c value of 1×10^5 A/cm^2 is attainable.

Strain dependences of NbN films on Hastelloy B substrates are given in Fig.8. These films were prepared under the deposition conditions optimized on B_{c2} and J_c.[16] The thicknesses of NbN layer are 300 and 700 nm. As can be seen in this figure, two films show little change in J_c at strains lower than 1 %. The value of irreversible strain limit ε_{irrev} in a 700 nm thick NbN film reaches about 1.3 %. When the applied strain increased to more than 1.3 %, the J_c did not recover for unloading. In the case of a 300 nm thick film, the value

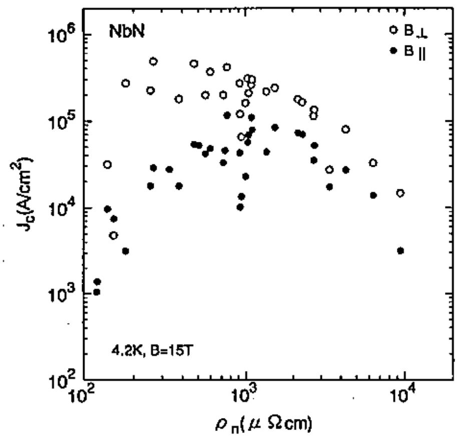

Fig.7 Critical current density of NbN films at 15 T as a function of normal state resistivity.

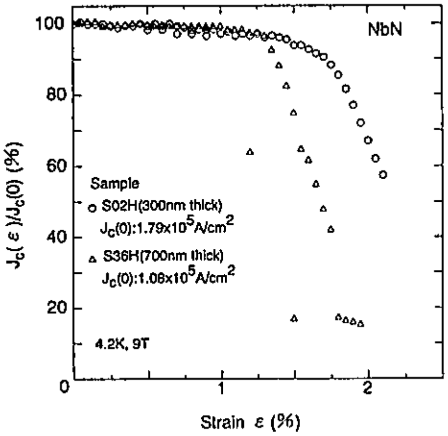

Fig.8 Critical current density of NbN films on Hastelloy B tape at 9 T as a function of tensile strain.

of ε_{irrev} seems to increase. The substrate material affects the strain dependence of J_c and ε_{irrev}. In NbN films on stainless steel substrates, values of ε_{irrev} are about 1 % lower than those for Hastelloy B substrates. The maximum of ε_{irrev} approaches 1.4 % in the case of Hastelloy B substrates.

IV. Summary

Sputtered films of Nb_3Ge with high T_c exhibit J_c exceeding 1×10^5 A/cm^2 at fields more than 20 T at 4.2 K. The J_c of CVD-prepared films is as high as that of sputtered films at fields up to 20 T. However, an marked decrease in J_c takes place in the field range of 20-25 T due to the lower B_{c2} character. The field dependence of J_c is much influenced by T_d. As T_d is increased to 900°C, anisotropy in J_c with respect to the applied field orientation appears. The B_{c2} of sputtered and CVD-prepared films is roughly proportional to their T_c and the highest value of B_{c2} at 4.2 K reaches 33.3 T in a sputtered film.

Sputtered NbN films have anisotropy in B_{c2}. This anisotropy produces strong anisotropy in J_c with respect to the field orientation. The J_c of the best film is higher than 1×10^5 A/cm^2 at fields up to 21 T for B⊥. The B_{c2} of films is related with ρ_n and increases with ρ_n in the range of below 500 μΩcm. High values of B_{c2}

are obtained in films with ρ_n higher than 500 μΩ cm. The strain dependence of J_c is influenced by the substrate material and NbN layer thickness. Films on Hastelloy B substrate maintain constant J_c at strains up to above 1 % at 4.2 K and 9 T. The maximum value of irreversible strain limit ε_{irrev} reaches 1.4 %.

Acknowledgments

The measurements of the field dependence of J_c and strain dependence of J_c were performed in the High Field Laboratory for Superconducting Materials, Tohoku University. We would like to thank members in HFLSM for their continuous support. Thanks are due to Prof. A. Nagata (Akita University) for help with the experiments on strain dependence. The data of B_{c2} measured in a pulsed field were taken mostly by Dr. G. Kido.

References

1) J.R.Gavaler, Appl.Phys.Lett.23(1973)480.
2) A.I.Braginski, G.W.Roland and A.T.Santhanam, IEEE Trans. Magn. MAG-15 (1979) 505.
3) K. Togano, H. Kumakura, T. Takeuchi and K. Tachikawa, IEEE Trans. Magn. MAG-19 (1983) 414.
4) K. Hamasaki, T. Inoue, T. Yamashita, T. Komata and T. Sasaki, Appl. Phys. Lett. 41 (1982) 667.
5) J. R. Gavaler, A. T. Santhanam, A. I. Braginski, M. Ashkin and M. A. Janocko, IEEE Trans. Magn. MAG-17 (1981) 573.
6) Dew-Hughes and R. Jones, Appl. Phys. Lett. 36 (1980) 856.
7) J.W.Ekin, J.R.Gavaler and J.Gregg, Appl.Phys.Lett.41(1982) 996.
8) M.Suzuki, N.Suzuki and T.Anayama, Jpn.J.Appl.Phys.21(1982) 840.
9) M. Suzuki, H. Ouchi and T. Anayama, Proc. Int. Cryo. Mater. Conf., ed. K. Tachikawa and A. Clark, Butterworths, Guildford (1982) 242.
10) M.Suzuki, H.Ouchi and T.Anayama, Jpn.J.Appl.Phys.22(1983)L307.
11) M.Suzuki, H.Ouchi and T.Anayama, Jpn.J.Appl.Phys.23(1984)991.
12) M. Suzuki, T. Anayama, G. Kido and Y. Nakagawa, J. Appl. Phys. 59 (1986) 975.
13) S. Foner, E.J.MacNiff, Jr., J.R.Gavaler and M.A.Janocko, Phys. Rev. Lett 47A (1974) 485.
14) M. Suzuki, M. Baba, M. Sato, T. Anayama, K. Watanabe and K. Noto,

Cryogenic Engineering 23(1988) 96. (in Japanese)
15)M. Suzuki, M. Baba and T. Anayama, Jpn. J. Appl. Phys. 26 Supple. 26-3 (1987) 947.
16)M. Suzuki, T. Kiboshi, T. Anayama and A. Nagata, Proc. of the MRS Int. Meet. on Advanced Materials 6 (1982) 77.