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NbN MATERIALS DEVELOPMENT FOR PRACTICAL SUPERCONDUCTING DEVICES

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NbN MATERIALS DEVELOPMENT FOR PRACTICAL SUPERCONDUCTING DEVICES*

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Abstract

Power switches such as a Superconducting Fault Current Limiter require large cross sectional area superconductors with both high critical current density J_c and normal state resistivity ρ_n. Large values of J_c and ρ_n have been previously reported in small cross cross sectional area "weak links" of NbN. We report on reactively sputtered NbN films up to 5 μm thick and 2.2 cm wide which have $\rho_n > 200$ μΩ cm and a self-field J_c up to 10^6 A/cm^2. Severe degradation in J_c was observed with increasing film width and for millisecond current pulses. This degradation could be substantially reduced by stabilization with either low ρ_n normal metal or the use of a sapphire substrate. The resistivity and critical current dependence both imply Josephson coupled grains and the results will be discussed within that model.

I. Introduction

Applications of superconducting technology have steadily increased in recent years. One of these is the proposal to limit power transmisison line fault currents with a superconducting power switch[1,2] which, when driven normal, commutates the fault current into an ambient temperature current limiting resistor. Design studies indicated the superconducting element should be a thin film deposited onto a flexible insulating substrate. The thin film with its large surface to volume ratio affords intimate contact with the helium coolant for stability, while the flexible substrate permits practical assembly of long lengths of superconducting element. There was also a need for large values of normal state resistivity ρn and critical current density J_c in order to minimize switch volume and keep the helium boil off low enough to permit fast reclosure of the circuit.

The choice of materials satisfying the above requirements is quite limited Most high T_c superconductors such as Nb_3Sn have high J_c's (>5 x 10^5 A/cm^2) but ρn's of less than 40 μΩ-cm. The only material reported in the literature with reasonably satisfactory properties is NbN with a transition temperature T_c up to 16.3 K, $J_c > 10^7$ A/cm^2, and ρ_n from 250-1000 μΩ-cm, although these[3,4] were obtained from very small cross-section constrictions. NbN has been prepared most successfully by a reactive sputtering process using an Nb target and a partial pressure of N_2 gas. In addition, it appeared that NbN could be successfully prepared at lower temperatures than other high T_c materials making the fabrication process considerably easier for long ribbons. All these factors led to NbN as the material most likely to achieve the design goal of $\rho_n \approx 300$ μΩ-cm and J_c of 3 x 10^6 A/cm^2.

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The purpose of this paper will be to present preliminary results of efforts to prepare thick, wide films of NbN on suitable substrates using reactive sputtering, characterize these films as to their superconducting properties and determine the sputtering parameters necessary to achieve the highest values of J_c and ρ_n. We will present evidence to suggest that the pinning mechanism in our samples is most likely Josephson coupling between grains and that the observed degradation in J_c for fast pulses and wide samples can be improved by thermal stabilization using high thermal conductivity sapphire substrates, or the more usual normal metal stabilization.

II. Sample Preparation and Characterization

a. Film Preparation.

Film preparation was carried out using a Varian 5" S-gun d.c. magnetron sputtering source mounted in a diffusion-pumped stainless-steel vacuum chamber. Substrates were supported from 3 to 6 inches above the gun on a large rotatable wheel designed to permit several samples close up to be made without breaking vacuum. 6 N's pure Argon was used as the sputtering gas at a typical pressure of 6 mTorr while N_2 from 0.1 to 1.5 mTorr was bled in using a separate leak valve. All pressures were monitored using an absolute pressure capacitance monitor. Substrate temperatures during preparation were the result of the sputtering process itself, and wre typically 150-250°C depending on target-substrate spacing. A small block heater was used when higher temperatures were needed. Substrates were either glass, fused quartz or sapphire with sample geometry established by in-situ masking or photolithography. There were a large number of sputtering parameters involved; nitrogen and argon pressures, the possible effect of impurity gasses, substrate material and temperature, film thickness and width and sputtering rate. To systematically proceed, it is desirable to relate the superconducting properties T_c, J_c, and ρ_n, and the structural properties including grain size, stoichiometry, crystal structure and structural disorder with the preparation conditions.

b. Superconducting properties.

It has been previously reported[5,6] that stoichiometry, structural phase and film morphology all depend on the nitrogen partial pressure and substrate temperature. The transition temperature T_c is sensitive to these properties since only the cubic phase of NbN has a high T_c(16.1 K) and deviations from stoichiometry, interstitial nitrogen, other phases, or structural disorder can reduce T_c. The data shown in Fig. 1 is an indication of film quality as a function of substrate temperature and nitrogen partial pressure. The need for increased N_2 partial pressures at higher substrate temperatures is presumably due to a decrease in the N_2 sticking coefficient as temperature goes up. Variations in the N_2 partial pressure and substrate temperature also affected ρ_n. As the N_2 partial pressure increased ρ_n increased, reaching values in our films of as high as 450 μΩ-cm with typical values being closer to 250-300 μΩ-cm. All

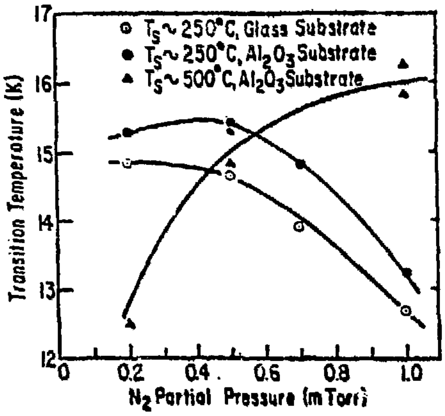

Fig. 1. The superconducting transition temperature T_c of NbN films as a function of nitrogen partial pressure and substrate temperature T_s for glass and sapphire substrates.

films prepared at 100-250°C substrate temperatures showed an increase in ρ_n with decreasing measuring temperature suggesting an activated conduction process. On the other hand, films prepared at ~ 500°C quite frequently showed a slight decrease in ρ_n with decreased temperature, suggesting metallic conduction in a disordered system.

The upper critical field $H_{c2}(0)$ has also been estimated by measuring $(dH_{c2}/dT)_{T \to T_c}$ in a perpendicular field and using the nonparamagnetically limited form of the Werthamer, Helfand, and Hohenberg equation.[7] Typical values of 35 Tesla(T) have been measured, similar to those obtained by Gavaler, et al.[4] but substantially higher than bulk values of ~ 15 T. These high values of $H_{c2}(0)$ have been attributed to the large ρ_n values found in NbN films. With the relationship derived from GLAG theory between $H_{c2}(0)$, ρ_n, γ(the electronic specific heat) and T_c, γ obtained from the literature, and our values of ρ_n and T_c, we get an $H_{c2}(0)$ of 35T, in close agreement with our previously determined value using the WHH formulation.

c. Structural Analysis.

The activated conduction observed in these films suggests a granular microstructure, that is, a network of small crystalline grains surrounded by voids, insulating materials, or absorbed gases such as excess nitrogen. Direct evidence for such a structure is difficult to obtain even with transmission electron microscopy. Some preliminary measurements on one of our films does show what appears to be void structures mixed in with very small grains, in agreement with the work of Wagner et al.[8]; who found columnar grains connected by narrow voids.

X-ray diffractometry was done on a number of as deposited films. The films exhibited the desired high T_c, fcc structure over the entire range of N_2 content with the lattice constant a_o varying from < 4.36 Å to 4.393 Å as the partial pressure varied from 0.5 mTorr to 1.5 mTorr, similar to the results of Wolf, et al.[9]. Bulk NbN has a lattice constant of 4.39 Å. There was some evidence for the Nb_2N hexagonal phase forming in very small amounts but only at high N_2 partial pressures.The high angle diffraction peaks were very weak and quite broad suggesting inhomogeniety and strain.

d. Macroscopic Imperfections.

Visual observations of the NbN samples revealed a macroscopic graininess to the surface. Optical and scanning electron microscopy showed a series of surface imperfections, mostly bumps, whose number density and size increased with increasing N_2 pressure. Energy dispersive x-ray analysis of the debris showed only an Nb peak. Whether the bumps contained N_2 was unclear because the analysis technique was insensitive to N_2. The origin of the surface bumps was suspected to be target spitting, i.e. macroscopic particles of target material ejected from the target surface during the sputtering process. To test this hypothesis, the target-substrate spacing was increased from 7.1 to 14.2 cm. The result should be a reduction in the number density of bumps due to gravitational effects on the more massive particles and a decrease in the number of particles per unit area impinging on the substrate resulting from the larger area being covered by the sputtered material. One micron thick film prepared at the larger distance showed almost complete elimination of surface bumps. As the film thickness increased, the number of bumps also increased, but was always less than the films made closer to the target. In addition, visual examination of the target-substrate space during sputtering showed many glowing particles being ejected from the target. Methods of completely eliminating target spitting have not been devised as the phenomenon appears to be directly related to the N_2 partial pressure. Measurements of J_c made on films with and without bumps revealed no significant differences leading to the conclusion that the problem is serious only for etched films.

e. Critical Current Density.

As previously indicated, the highest possible values of self-field J_c in liquid He at 4.2 K are desired, preferably > 3 x 10^6 A/cm^2. A variety of films thicknesses to 5 μm and widths up to 2 cm were prepared on glass substrates at ∿ 250°C. For one series of samples as film thickness increased from 0.5 to 3.5 μm, J_c decreased from 1.5 x 10^6 A/cm^2 to 5 x 10^5 A/cm^2 and it was found to be generally true with all samples that J_c was less for thicker films. In addition, measurements of J_c as a function of film width also indicated an order of magnitude decrease in J_c as width went from 0.5 to 2 cm. These results are a factor of ten lower than Gavaler had measured for very small area constrictions[4] and, under best case conditions, a factor of two lower than our minimum needs. More significantly, the further decrease in J_c for thick, wide films could have serious consequences on the fault current limiter design, which dictated thick (5 μm), wide (10 cm) films to meet overall current carrying requirements during normal operation. These results led to an analysis of the causes of width (w) and thickness (d) dependence along with possible remedies.

Three possible causes of the decrease of J_c with d have been considered. Two relate to grain size which can vary with thickness and the third to an increase in self-magnetic field as the total current increases with thickness. In the self-field model, if we assume the current distribution is independent of J_c and d << w, then to a good approximation the self-field B at any point depends only on total current, or for constant w, B ∝ Jd. Breakdown occurs at a critical $\vec{J} \times \vec{B}$ which implies $J_c^2 d$ is a constant. Calculation of this product from experimental results at constant w indicates a variation of at least a factor of two suggesting poor agreement with the model.

Grain boundary pinning has been generally accepted as a valid pinning mechanism in superconductors. Here the critical value of the product $\overline{J} \times \overline{B}$ ($= J_c^2 d$) is not constant but proportional to the grain boundary area per unit volume, which depends inversely on the average grain diameter a_o. This model predicts $J_c^2 da_o$ is a constant, but has not been checked due to lack of accurate grain diameter values for different thicknesses. The other model involving grain size is that of Josephson coupling between grains. This concept and the evidence to support it will be treated in detail in a subsequent section.

III. Stabilization

The decrease in J_c with increasing width and for short current pulses suggested an instability problem in the NbN films. Instability and subsequent breakdown can occur when a hot spot develops due to the local critical current being exceeded or sudden magnetic flux motion which dissipates heat. The traditional method of treatment is to place a high electrical and thermal conductivity material such as copper in direct contact with the superconductor. Flux motion is reduced by eddy current damping from the normal metal, while a local normal region in the superconductor can be given time to recover if the current temporarily shifts to the normal metal. Hot spots can be kept from growing because the normal metal is an excellent thermal conductor which rapidly removes heat from a localized area, spreads it over a large region and ultimately dumps it into the helium bath, permitting recovery of the superconductor. The main disadvantage of normal metal stabilization is its very low electrical resistance which reduces the overall efficiency of a power switch.

a. Normal Metal Stabilization.

To ascertain the effectiveness of normal metal stabilization, 6–10 μm of high purity Cu was deposited directly onto NbN films. J_c's were measured and compared with uncoated films prepared at the same time. The results are shown in Fig. 2 for both pulsed and dc currents. Pulsed currents were used to simulate the actual operation of a 60 Hz power switch. It is quite evident that after an initial drop in J_c, there is very little additional decrease for stabilized films, attesting to the effectiveness of the Cu films. It is not clear, however, which of the previously discussed stability mechanisms are important.

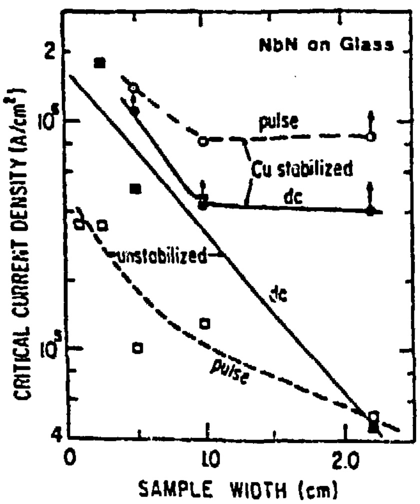

Fig. 2. The effect of copper stabilization of NbN on glass. The Cu reduced the differences between pulsed and dc operation and, for the most part, eliminated the width dependence. The arrows (↑) indicate where higher values of J_c would have been achieved, was not the current capability of the power supply exceeded.

b. Sapphire Stabilization.

Measurements previously made in our laboratory on Nb_3Sn films deposited onto sapphire substrates without metallic stabilization showed no J_c width dependence for pulsed and dc currents. This suggested the possibility that the excellent low temperature thermal conductivity of sapphire was effective in dissipating heat from local hot spots. To test this concept a series of 1μm thick NbN films of different widths were deposited onto sapphire substrates. The critical currents for pulses (open squares) and dc (solid squares) are shown in Fig. 3. The values of J_c range between $1\text{–}2 \times 10^6$ A/cm^2, are almost independent of width although the pulsed values are somewhat lower. It is clear, however, that these results are significantly better than unstabilized NbN on glass and roughly equivalent to NbN samples stabilized with copper. These NbN films were subsequently overcoated with 10–15 μm of Cu, remeasured and plotted in Fig. 3 for comparison. As can be seen, the normal metal provided virtually no improvement in the dc J_c whereas the low pulsed J_c values were improved somewhat. The obvious conclusion is that thermal stability is the important stability mechanism for NbN films and not eddy current damping of flux jumps or current sharing. This is of great significance to a power switch design because the insulating sapphire substrate will not reduce switch efficiency as a low ρ_n normal metal stabilizer would.

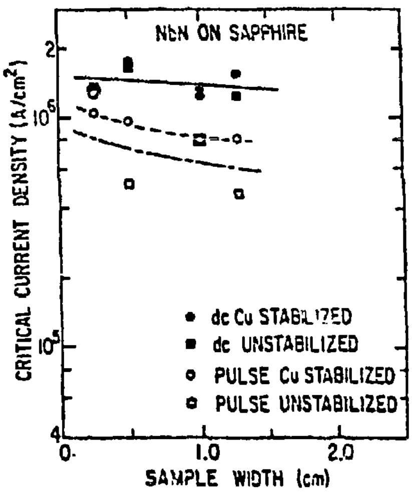

Fig. 3. The effects on J_c for NbN on sapphire with and without Cu stabilization. Sapphire substrates almost completely solve the stabilization problem. The addition of copper has little effect.

IV. Josephson Coupling

The results presented so far suggest that although ρ_n can be made sufficiently high, J_c for all NbN samples did not exceed 2×10^6 A/cm^2 whether stabilized or not. The mechanism(s) governing J_c must be understood in order to choose appropriate avenues of improvement. In section III, several pinning mechanisms were outlined including Josephson coupling of grains. In this model it is assumed that the NbN films contain grains of diameter a_o in the plane of the film and that these grains are weakly coupled to each other thru small metallic bridges (weak links) or thin insulating layers. Normal conductivity is by thermally activated hopping from grain to grain and superconductivity is due to Josephson coupling between grains. The normalized resistance vs temperature curve shown in the insert of Fig. 4 is supportive of a thermally activated process. Additional evidence for Josephson coupling is given by the temperature dependance of J_c near T_c as shown in Fig. 4. Near T_c the Josephson relation for I_c predicts $J_c \propto (T_c - T)$, in reasonable agreement with Fig. 4. On the other hand grain boundary pinning of flux lines in high T_c films is characterized by a $(T_c - T)^2$ dependence of J_c which is a much poorer fit to the data.

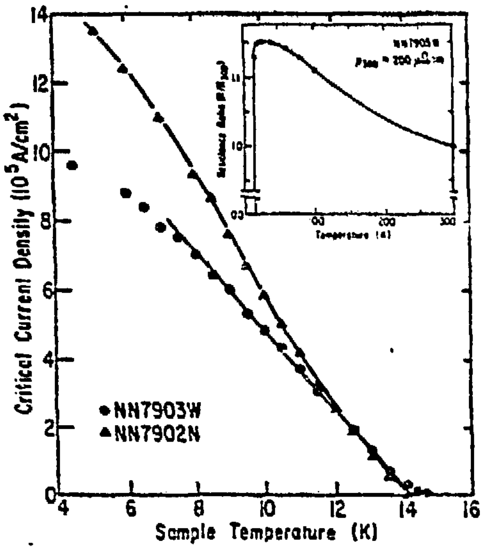

Fig. 4. J_c vs. T for two NbN samples. Both were made at a nitrogen partial pressure of ~0.6 mTorr and T_s ~250°C. T_c was ~14.6 K, and thickness ~3 μm. The insert shows the resistance ratio vs. temperature for one of the samples.

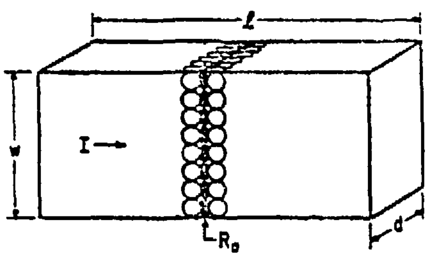

Fig. 5. The schematic model used to derive a relationship for J_c based on Josephson coupling between spherical grains. Here w is the film width, d is thickness and ℓ is the length. R_o is the total parallel resistance of all the junctions in one plane.

A relationship between J_c and grain diameter a_o can be obtained using the model shown in Fig. 5. The grains can be columnar or spherical. For simplicity assume a three dimensional grid of grains of diameter a_o on a cubic lattice and neglect current flow lateral to the net current flow. J_c can be calculated by lumping together all the junctions in a plane perpendicular to the current flow. I_c is given be the well known expression[10] $I_c = [\pi\Delta(T)/2R_o]\tanh[\Delta(T)/2kT]$, where $\Delta(T)$ is the temperature dependent energy gap, and R_o is the total parallel resistance of the junctions in a plane. At 4.2 K, $\Delta(T) \sim \Delta(T = 0) = \Delta(0)$ and $\tanh[\Delta(0)/2kT] \sim 1$, so that $J_c = I_c/dw = \pi\Delta(0)/2R_o dw$. The total resistance of a film of length ℓ will be given by the series sum of ℓ/a_o junctions or $R = R_o\ell/a_o$. By definition $R = \rho_n\ell/dw$ giving $J_c = \pi\Delta(0)/2\rho_n a_o$. Using a ρ_n of 250 μΩ-cm and $J_c = 1.3 \times 10^6$ A/cm^2 from one of our samples (NN7909), and an estimated $\Delta(0) = 2.7$ mV based on a 15 K T_c, we get $a_o = 1300$Å. SEM's of this sample show columns of ~ 1000 Å diameter indicating reasonable agreement with theory.

An obvious objection to this model is whether the very high critical fields for such films are compatible with Josephson coupling since it is well-known that a few gauss can affect the phase coherence across a typical Josephson junction between two films. The Josephson critical current as a function of field is[11] $J_c(H) = J_c(0)|\sin x/x|$, where $x = \pi\phi/\phi_o$, ϕ is the flux threading the junction and ϕ_o is the flux quantum. Therefore J_c is decreased for $\phi \gtrsim \phi_o$, and the corresponding field is given by ϕ_o/A where A is the junction area. For the case of NbN films $H_{c2}(0) = 35$T implying a junction area of 10^{-12} cm^2 or ~ 100 Å diameter. This is not incompatible with the possible coupling between grains previously discussed. The model predicts that J_c can be increased by decreasing the grain size.

V. Conclusions

We have shown that thick wide films of NbN can be produced by magnetron reactive sputtering. The decrease of J_c with short current pulses and increasing width can be substantially reduced by normal metal stabilization and, more importantly for switch applications, the use of sapphire substrates. J_c measurements are consistent with a Josephson model for coupling between grains as well as grain boundary pinning if we ignore the $J_c(T)$ dependence and predicts increased values of J_c as the grain size is reduced. Efforts to improve J_c by reducing grain size are part of our continuing program.

VI. Acknowledgements

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