ION-BEAM DEPOSITION OF NbN_xC_y THIN FILMS FOR MICROELECTRONIC APPLICATIONS

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Abstract

We have fabricated high quality superconducting NbN_xC_y thin films using a low-energy dual ion-beam fabrication method. In this method, one ion beam sputters Nb to the substrate while the second beam bombards the growing film with low energy (~100 eV) N_2+CH_4 ions. The use of methane as a source of carbon is essential for this method. NbN_xC_y thin films fabricated in this way have T_c up to 13.2K, resistivity ~80-120 μΩcm, residual resistance ratio ~1.0 and calculated magnetic penetration depths <285 nm. These films are deposited on Si wafers which are not intentionally heated or cooled. Electronic tunneling studies indicate that these films are strong coupled superconductors ($2\Delta/kT_c \leq 4.0$) with superconducting energy gaps up to 2.43 meV. NbN_xC_y/native oxide/Pb-alloy junctions have properties suitable for SIS mixer applications.

Introduction

Since the early 1980s it has been clear that NbN is an excellent candidate for superconducting microelectronic applications.[1] NbN is a refractory, chemically inert material with high T_c (up to 17K). NbN-NbN SIS junctions can be operated in a commercial cryo-cooler (at ~10K) and can withstand thermal cycling. SIS junctions made with NbN and a soft counter electrode are being studied for use as high T_c SQUIDs and in Josephson LSI circuits.[2] Furthermore, NbN_x thin films can be fabricated on low temperature substrates (<100 °C) in a standard vacuum system (background pressure ~10^{-7} Torr).[3,4,5]

The use of a dual ion-beam sputtering method for making compounds was initiated by Weissmantel,[6] followed by Harper et al.[7] We have adopted it for the first time to fabricate superconductors. In the dual ion-beam method, one ion source sputters Nb atoms from a Nb target to the substrate while the second ion source provides N_2+CH_4 ions to the growing film. Depending on the beam voltage of the second ion source, this method may be gentler than higher pressure (~10^{-2} Torr) sputtering methods. The low sputtering pressure of the dual ion-beam method allows the ion beam to be directional and the flux to be easily adjusted. Moreover, the bombardment of the growing films with low-energy ions provides energy sufficient to optimize film quality (e.g., T_c, stress) without degrading underlying structures.

We began in 1984 the work of fabricating superconducting NbN_x (δ-phase NbN, B1 crystal structure) using a dual ion-beam sputtering method.[8] Our work was directed towards microelectronic applications, primarily SIS quantum mixers. Since then, we have fabricated excellent quality NbN_xC_y films with moderately high T_c (~13.2K) on near-room-temperature Si substrates.[9] Methane is essential for producing the highest T_c films. Our NbN_xC_y films have been tested in large area SIS tunnel junctions with PbBi alloy counter electrodes. These NbN_xC_y/native oxide/Pb_zBi_{1-z} (z=1 or 0.95) junctions are reasonably rugged, and are readily made. We believe they have good potential for use as SIS mixers. Work in this area is currently underway in this lab.[10]

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In this paper, we report the use of dual ion-beam deposition to fabricate NbN_xC_y thin films. We report the properties of the high T_c (~13.2K) films, and give preliminary results on all-refractory NbN-NbN and NbN-Nb junctions.

Dual Ion-Beam Deposition

Our sputtering configuration is shown in Fig. 1. The first ion source[11] is mounted on the top plate of a pyrex vacuum chamber and faces a multiple target holder. This ion source uses Xe ions to sputter Nb atoms to the substrate. Using this single ion beam alone, high quality superconducting Nb thin films (~9.1K)[12] and artificial tunnel barriers[13] have been produced. The second ion source[14,15] is mounted onto the bottom plate and discharges N_2, CH_4 and/or Ar ions to the substrate. When the two ion sources are operated simultaneously, smooth and shiny NbN_xC_y thin films are formed on near-room-temperature Si substrates. These substrates are scribed from air-oxidized Si wafers of either (100) or (111) orientation. The temperature of the substrate holder is <60 °C.

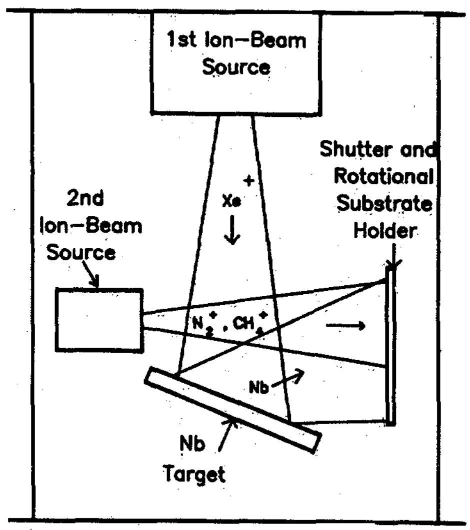

Fig. 1. Schematic diagram of dual ion-beam sputtering system.

The beam energy and flux of the first ion source are fixed at 1500 eV and 34 mA, respectively. The beam energy and flux of the second ion source are varied for optimum film quality. Fig. 2 displays the sputtering conditions and corresponding superconducting transition temperatures, T_c, of a set of NbN_xC_y films. When the substrate is not heated, the highest T_c (~13.2K) is obtained using low energy ions from the second source.

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T_c as a function of beam voltage of the 2nd source exhibits a maximum around 50-100 V. For high energy (1000-1500 eV) fabrication, the addition of CH_4 does not improve T_c significantly, but improves the operational stability of the 2nd source. For low energy fabrication, on the other hand, T_c improves with an increasing fraction of CH_4 in the discharge until a CH_4/N_2 ratio of ~1.

Maximum T_c is achieved with a beam current (ion flux) for the 2nd ion source of 6.3 mA for low-energy (100 eV) operation, and 3 mA for high-energy (1500 eV) operation. The sputtering pressure for the 2nd source is ~1×10^{-4} Torr. The NbN_xC_y formation rate is 1.2-1.7 Å/s while the Nb deposition rate is 2.0-2.3 Å/s. Heating the substrate to 200 °C increases T_c by 1 °C (see the stars in Fig. 2). The film thicknesses are 1000 Å and 3000 Å, respectively, for the low-energy and high-energy fabrication. It is clear that low-energy dual ion-beam fabrication produces films with higher T_c than the high-energy method.

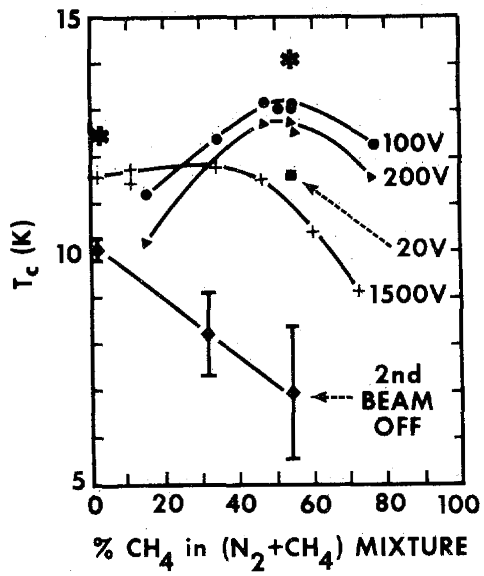

Fig. 2. T_c as a function of molecular % CH_4 in (N_2+CH_4)mixture for different beam voltages of the second ion source. (+) fabrication with 1500 eV N_2 or N_2+CH_4 ions; (▲) fabrication with 200 eV N_2+CH_4 ions; (●) fabrication with 100 eV (or 50 eV) N_2+CH_4 ions; (■) fabrication with 20 eV N_2+CH_4 ions; (◆) fabrication with first ion source alone in a N_2 or N_2+CH_4 partial pressure of ~1×10^{-4} Torr; (*) T_c of films fabricated with 200 °C substrate temperature. With a single ion beam and an N_2 atmosphere or N_2 in the discharge, T_c values up to 11-12K are obtained for N_2 or N_2+CH_4 partial pressure >1×10^{-4} Torr. However, in all cases of single ion-beam deposition, multiple or broad transitions are obtained.

Some of the attempts at single ion beam fabrication (2nd beam off) of NbN_xC_y are also shown in Fig. 2. Those films were produced while sputtering Nb in an atmosphere of N_2 or a N_2+CH_4 mixture. The total N_2 or N_2+CH_4 pressure is ~1×10^{-4} Torr. Although T_c can be improved somewhat by increasing the N_2 pressure, it is always well below that obtained using the 2nd ion source. Furthermore, films produced with a single ion source show multiple or broad transitions, and the films are highly stressed (flaky or non-smooth) and of poor quality. Even though the visual appearance of these films can be improved by pre-sputtering the Si substrate with N_2^+, by addition of CH_4 during sputtering, or by elevating the substrate temperature slightly, the presence of the broad, multiple transitions remains. Similar T_c and film quality are obtained by sputtering Nb with Xe+N_2 ions.

Film Properties

We have used the following methods to study the properties of our NbN_xC_y films: van der Pauw four-probe method for T_c and resistivity (ρ); transmission electron microscopy (TEM) for grain size, crystallographic orientation and lattice constant (a_o); Auger depth profile and x-ray photoelectron spectroscopy (XPS) for compositional analysis; electron tunneling with Pb or PbBi alloy counter electrodes on native oxide barriers to study the superconducting properties.

NbN_xC_y films produced with the low energy (100 eV) dual ion-beam method (T_c~13.2K) show excellent electrical properties (see Table I). Typical resistivity is <120 μΩcm with residual resistance ratio (RRR = ρ(300K)/ρ(20K)) ~1.0. Previously, such low resistivities (~80 μΩcm) have not been achieved without substantial heating of the substrate.[16,17] The RRR value of 1.0 indicates weak metallic behavior; this also has not been achieved in most studies. Using an approximation derived for dirty superconductors[18] and a $2\Delta/kT_c$ value of 3.9, the calculated magnetic penetration depth λ ($\propto \rho(T_c)^{-1/2}$) for these films (<285 nm) is approaching the intrinsic value of 200 nm,[17] even without intentional substrate heating.

Fig. 3 shows a dark field TEM micrograph and a TEM diffraction pattern of a typical film. The NbN_xC_y grain size is < 50 Å. Small grains in refractory materials are usually associated with low substrate temperature during deposition; this has been seen in previous work on NbN.[3,4,5] The value of the lattice constant a_o obtained from the TEM diffraction pattern is >4.38 Å and can be as high as 4.46 Å. This indicates that some of the carbon may be contained in the films interstitially. The strongest electron diffraction peak occurs for the (220) plane. This may result from a preferential growth of δ-phase NbN (NaCl-type structure) caused by the directionality of the ion-beam,[19] or from a mixture of δ-phase and tetragonal crystal structures.[20] Auger depth profiles show a nearly constant Nb/N/C ratio throughout the thickness of the films (~1000 Å). Large amounts of carbon were found in several films. A typical Nb/N/C atomic ratio is ~1/0.6/0.6. We infer from these ratios that most of the carbon is contained in the films substitutionally.

TABLE I. V_{beam2} is the beam energy of the second ion source. I_{beam2} denotes the total ion current from the second ion source.*: N_2/Ar mixture, with flow rates of 2.1/0.57sccm. The magnetic penetration depth λ is calculated with the equation given in Ref. 5 using a $2\Delta/kT_c$ value of 3.9. The atomic composition ration is from Auger depth profile analysis. a_o denotes lattice constant. Diff. denotes the strongest diffraction plane with electron beam diffraction. Typical film thickness is 1000 Å.

Sample	V_{beam2} (V)	I_{beam2} (mA)	P_{N_2} (μTorr)	N_2/CH_4 flow (sccm)	T_c (K)	δT_c (K)	ρ(20K) (μΩcm)	RRR	λ (nm)	Nb/N/C ratio	a_o (Å)	Diff.
A	1500	3.1	58	2.1/0.34	11.7	0.10	120	0.89	320	1/0.92/0.68	4.38	(200)
B	1000	4.1	58	*	11.2	0.09	158	0.92	375	1/0.94/0.17	-	-
C	200	6.4	42	1.5/2.5	12.4	0.06	156	0.99	356	1/0.64/0.64	-	-
D	100	6.3	42	1.5/2.5	12.7	0.09	77	1.02	246	1/0.60/0.88	4.41	(220)
E	≲ 100	6.2	42	1.5/2.5	13.0	0.16	105	1.01	284	1/0.60/0.59	4.46	(220)

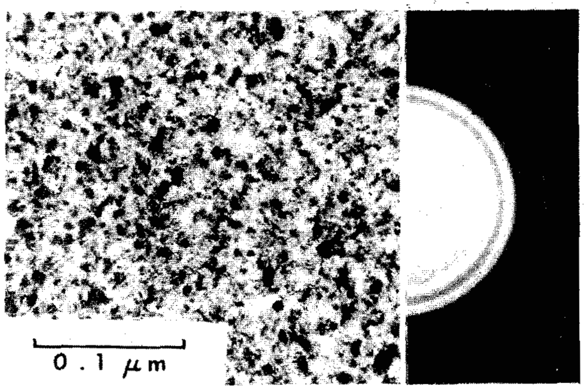

Fig. 3. TEM micrograph and TEM diffraction pattern of a NbN_xC_y film (~570 Å thick) fabricated with the same parameters as sample A in table I.

Electron tunneling studies indicate that these NbN_xC_y films are strongly coupled superconductors with $2\Delta/kT_c$ values of 3.8-4.0. For these films, Δ_{NbNC} increases from ~2.0 meV to 2.43 meV when T_c increases from 12.6K to 14.1K. Most junctions exhibit a Josephson critical current at ambient magnetic field which is reduced below the maximum possible value. Thermal noise may also have depressed the measured critical current. Fig. 4 shows an I-V curve of a large area (3.2×10^{-4} cm^2) NbN_xC_y/native oxide /$Pb_{0.95}Bi_{0.05}$ tunnel junction at 4.5K. The NbN_xC_y base electrode has a T_c =12.7K and a Δ_{NbNC} ~2.0 meV. The sharpness of the current rise (width ~0.13 mV) at the gap voltage may be due to a junction heating effect caused by the small tunneling resistance (~0.05 Ω). The current rise at the sum-gap is ~50 mA which implies a maximum critical current density of ~160 A/cm^2 for an ideal junction. The tunnel conductance at 2mV (σ(2mV)) is ~5% of the tunnel conductance at 5 mV (i.e., σ(2mV)/σ(5mV) = (I(2mV)/I(5mV))x2.5 ~0.05). The BCS sub-gap current from thermal excitation at 4.5K is ~2% of the tunneling current for this junction. Fig. 5 is an I-V curve of a large area NbN_xC_y/native oxide/Pb tunnel junction at 2K. The NbN_xC_y base electrode was fabricated at 200 °C substrate temperature and has T_c =14.1K. Its Δ_{NbNC} is 2.43 mV. The width of the current rise for this I-V is 0.27 mV, which is typical for our NbN_xC_y films. The current rise at sum-gap is ~8 mA, which corresponds to a maximum critical current density of ~25 A/cm^2. The leakage current at 2 mV is ~1.4% of the tunneling current at 5 mV. The BCS sub-gap current is ~0.02% of the tunneling current. Both tunneling oxides are formed by air oxidation of NbN_xC_y for ~20 minutes. We conclude that NbN_xC_y native thermal oxide can be easily produced, and gives low junction resistances, <1.6 mΩcm^2.

All Refractory SIS Tunneling

We have attempted to fabricate NbN-NbN and NbN-Nb junctions. The NbN_xC_y native oxides are destroyed by the deposition of refractory metals, either Nb or NbN. All junctions exhibit superconducting shorts, probably caused by pin holes in the tunnel barrier. The use of the 2nd ion source does not seem to be responsible for the poor quality of the NbN-NbN junctions, since the 2nd source is inoperative during the Nb deposition for NbN-Nb junctions, and their quality is equally poor.

Several attempts have been made at fabricating NbN-NbN or NbN-Nb junctions with artificial barriers. The artificial barriers considered are thermal oxides of Al, Ta and Mg overlayers and ion-beam oxidized Nb_xO_y, Al_xO_y, and Ta_xO_y. The ion-beam parameters used are 100 eV and 1-5 mA for 1-5 minutes. Most of these junctions show superconducting shorts with varying degrees of non-linear features. Among all these junctions, the most promising oxides for NbN-NbN junctions are ion-beam oxidized Al_xO_y and Nb_xO_y. Futher study is necessary for making high T_c NbN-NbN junctions using a dual ion-beam method.

We should mention that Shoji et al. have recently successfully fabricated 14.5K NbN-NbN SIS junctions with no obvious gap depression.[21] (All previously reported NbN-NbN SIS junctions had reduced gap values in the counter electrodes.) We believe their work has demonstrated the possibility of using high T_c NbN-NbN junctions for superconducting LSI circuits.

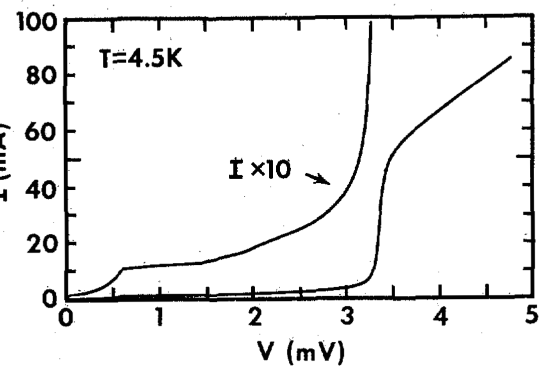

Fig. 4. I-V curve of a NbN_xC_y/native oxide/$Pb_{0.95}Bi_{0.05}$ junction at T ~4.5K. The base electrode NbN_xC_y has T_c = 12.7K. The sum-gap voltage is 3.35 meV and the width of the current rise is ~0.13 mV. Tunneling resistance is ~0.05 Ω. The Δ_{NbNC} is ~2.0 meV.

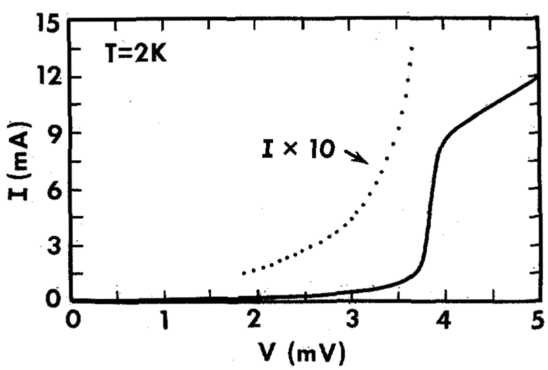

Fig. 5. I-V curve of a NbN_xC_y/native oxide/Pb junction at T = 2.0K. T_c of the base electrode, which is deposited at 200 °C substrate temperature, is 14.1K. The sum-gap voltage is 3.83 mV and the width of the current rise is 0.27 mV. The Δ_{NbNC} is ~2.43 meV.

Discussion

At this point, one can only speculate as to the mechanism of film formation in the dual ion-beam method. The N_2^+ ions may pick up an electron after impacting with the Si substrate (grounded) and then incorporate with the Nb atoms into the growing film. Alternatively, the N_2^+ ions may excite other N_2 molecules into excited electronic states (the excitation energy required is on the scale of a few eV); these could then dissociate yielding N atoms which can readily form compounds with Nb. Presumably, much of the ion energy is dissipated in the film as heat. From the fact that the growth rate (~1.7 Å/s) in the low-energy fabrication method is about the same as that obtained when fabricating NbN_x with the single ion-beam source alone, it appears that a major function of the N_2 and CH_4 ions is to provide energy locally at the surface of the growing film. However, Fig. 2 shows that too much ion energy may be undesirable. Films fabricated with high energy N_2 (and/or CH_4, or Ar) ions have higher resistivity and lower T_c. This suggests that the impact of 1000-1500 eV ions may be disturbing or damaging the existing layers of the growing NbN_xC_y film. Damage to the films caused by ion impact may also be the reason for the non-ideal (<17K) T_c of films fabricated in the low-energy method, although this could also be caused by oxygen contamination due to low film growth rate. Based on the above observations, we speculate that surface-heating with an infrared laser (possibly used in conjunction with extremely low-energy ions from the 2nd source) might be an interesting alternative to the present ion bombardment method from the 2nd ion source. With such an approach there would not be large momentum transfer to damage the layers already formed. A higher Nb deposition rate may also improve T_c.

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