ION-BEAM DEPOSITION OF NbNxC films for microelectronic applications

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Abstract

We have fabricated high quality superconducting NbNxC 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) N2 or CH4 ions. The use of methane as a source of carbon is essential for this method. NbNxC films fabricated in this way have Tc 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 (2Δ/κ ≈4.0) with superconducting energy gaps up to 2.43 meV. NbNxC/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 Tc (up to 13.2K). NbN-NbN SIS junctions can be operated in 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 Tc SQUIDs and in Josephson LSI circuits.2 Furthermore, NbN 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 N2 or CH4 ions to the growing film. Depending on the beam voltage of the second ion source, this method can 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., Tc, stress) without degrading underlying structures.

We began in 1984 the work of fabricating superconducting NbN (β-phase) thin films. Our work was directed towards microelectronic applications, primarily SIS quantum mixers. Since then, we have fabricated excellent quality NbNxC films with moderately high Tc (~13.2K) on near-room-temperature Si substrates.8 Methane is essential for producing the highest Tc films. Our NbNxC films have been tested in large area SIS tunnel junctions with PbI alloy counter electrodes. These NbNxC/Native oxide/PbI2-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.9

In this paper, we report the use of dual ion-beam deposition to fabricate NbNxC thin films. We report the properties of the high Tc (~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 source10 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 barriers13 have been produced. The second ion source14 is mounted onto the bottom plate and discharges N2, CH4 and/or Ar ions to the substrate. When the two ion sources are operated simultaneously, smooth and shiny NbNxCy 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.

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, Tc, of a set of NbNxC films. When the substrate is not heated, the highest Tc (~13.2K) is obtained using low energy ions from the second source.
Fig. 2, as a function of molecular % CH₄ in (N₂+CH₄) mixture for different beam voltages of the 2nd ion source. (+) fabrication with 1500 eV N₂ or N₂+CH₄ ions; (A) fabrication with 200 eV N₂+CH₄ ions; (B) fabrication with 100 eV (or 50 eV) N₂+CH₄ ions; (■) fabrication with first ion source alone in a N₂ or N₂+CH₄ partial pressure of ~1x10⁻⁴ Torr; (*) fabrication with 200 °C substrate temperature. With a single ion beam and an N₂ atmosphere or N₂ in the discharge, Tc values up to 11-12K are obtained for N₂ or N₂+CH₄ partial pressure ~1x10⁻⁴ Torr. However, in all cases of single ion beam deposition, multiple or broad transitions are obtained.

**TABLE I**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Vbeam₁ (V)</th>
<th>Ibeam₁ (mA)</th>
<th>Pₙ₂ (mTorr)</th>
<th>N₂/CH₄flow (sccm)</th>
<th>Tc (K)</th>
<th>δTc (K)</th>
<th>ρ(20K) (μΩcm)</th>
<th>RRR</th>
<th>λ (nm)</th>
<th>Nb/N/C</th>
<th>p₀ (Å)</th>
<th>Diff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1500</td>
<td>3.1</td>
<td>58</td>
<td>2.1/0.34</td>
<td>11.7</td>
<td>0.10</td>
<td>120</td>
<td>0.89</td>
<td>320</td>
<td>1/0.2/0.68</td>
<td>4.38 (200)</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>1000</td>
<td>4.1</td>
<td>58</td>
<td>-</td>
<td>11.2</td>
<td>0.09</td>
<td>158</td>
<td>0.92</td>
<td>375</td>
<td>1/0.04/0.17</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>200</td>
<td>6.4</td>
<td>58</td>
<td>13/25</td>
<td>12.4</td>
<td>0.06</td>
<td>156</td>
<td>0.99</td>
<td>356</td>
<td>1/0.04/0.04</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>100</td>
<td>6.5</td>
<td>42</td>
<td>15/25</td>
<td>12.7</td>
<td>0.09</td>
<td>77</td>
<td>1.03</td>
<td>246</td>
<td>1/0.0/0.08</td>
<td>4.41 (220)</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>≤100</td>
<td>6.2</td>
<td>42</td>
<td>15/25</td>
<td>15.0</td>
<td>0.16</td>
<td>105</td>
<td>1.03</td>
<td>284</td>
<td>1/0.0/0.09</td>
<td>4.48 (220)</td>
<td></td>
</tr>
</tbody>
</table>

Some of the attempts at single ion beam fabrication (2nd beam off) of NbN/C, are also shown in Fig. 2. Those films were produced while sputtering Nb in an atmosphere of N₂ or a N₂+CH₄ mixture. The total N₂ or N₂+CH₄ pressure is ~1x10⁻⁴ Torr. Although Tc can be improved somewhat by increasing the N₂ 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 N₂⁺, by addition of CH₄ during sputtering, or by elevating the substrate temperature slightly, the presence of the broad, multiple transitions remains. Similar Tc and film quality are obtained by sputtering Nb with Xe+N₂ ions.

**Film Properties**

We have used the following methods to study the properties of our NbN/C films: van der Pauw four-probe method for Tc and resistivity (ρ); transmission electron microscopy (TEM) for grain size, crystallographic orientation and lattice constant (a₀); 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/C films produced with the low energy (100 eV) dual ion-beam method (Tc-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. In contrast, this RRR value of 1.0 indicates weak metallic behavior; this has not been achieved in most studies. Using an approximation derived for dirty superconductors and a 2A/kTc value of 3.9, the calculated magnetic penetration depth λ (~p(Tc)/2A) for these films (~285 nm) is approaching the intrinsic value of 200 nm, even without intentional substrate heating.

Fig. 3 shows a dark field TEM micrograph and a TEM diffraction pattern of a typical film. The NbN/C 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. The value of the lattice constant a₀ 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 6-phase NbN (NaCl-type structure) caused by the directionality of the ion-beam, or from a mixture of 6-phase and tetragonal crystal structures. 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.
Electron tunneling studies indicate that these NbN_xC_y films are strongly coupled superconductors with 2Δ/E_C^* values of 3.8-4.0. For these films, ΔNbNC increases from ~2.0 meV to 2.43 meV when T increases from 12.6K to 14.5K. 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 junction at 4.5K. The NbN_xC_y base electrode has a T_c = 14.1K. Its ΔNbNC is 2.43 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 (of 2mV) is ~5% of the tunnel conductance at 5 mV (i.e., g(T=2mV)/g(T=5mV) = (I(2mV)/I(5mV))×2.5 ~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 ΔNbNC is 2.43 meV. 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 ~35 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. 

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 Nb-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_0.95Si_0.05. The ion-beam parameters used are 160 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_0.95, and Nb_0.95. Further 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 (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. 

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**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. 

**Fig. 4.** I-V curve of a NbN_xC_y/native oxide/Pb_0.95Si_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 ΔNbNC is ~2.0 meV. 

**Fig. 5.** I-V curve of a NbN_xC_y/native oxide/Pb_0.95Si_0.05 junction at T = 2K. The base electrode NbN_xC_y has T_c = 14.1K. The sum-gap voltage is 3.83 meV and the width of the current rise is ~0.27 mV. The ΔNbNC 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 Nb atoms may pick up an electron upon 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 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 $N_2$ (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$_x$ 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 ion deposition 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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Reference