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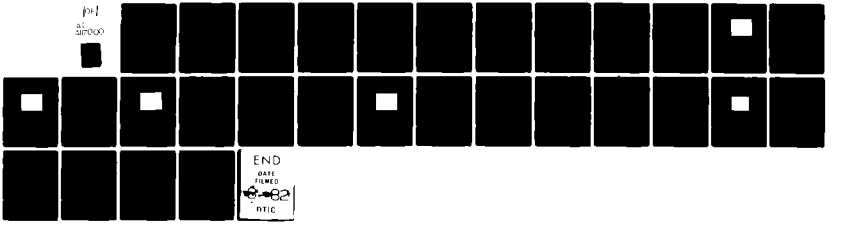

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FINAL REPORT FOR
SUPERCONDUCTIVE NIOBIUM OXIDE
TUNNEL DEVICE PROGRAM

Prepared for:

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15 April 1982

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Final Report for Superconductive Niobium Oxide

Tunnel Device Program

Introduction

The purpose of this program was to develop the technology for the fabrication of small-area Josephson tunnel junctions with niobium electrodes for use as microwave detectors and mixers. Junctions approximately 2 μm square were to be made. Niobium-niobium oxide-lead junctions were used to establish processes for sputter cleaning and sputter oxidizing the niobium base electrode. When these processes were established, niobium-niobium oxide-niobium junctions were made by sputtering the base electrode, sputter cleaning and sputter oxidizing the base electrode in a sputter deposition system with backsputter capability, and evaporating the upper electrode in an electron-beam evaporation system. Experiments were also done to make junctions with aluminum-oxide barriers.

The report is divided into seven parts: (1) vacuum systems, (2) masks for photolithography, (3) processing techniques, (4) niobium-niobium oxide-lead junctions, (5) niobium-niobium oxide-niobium junctions, (6) niobium-aluminum oxide-aluminum-niobium junctions, (7) summary and conclusions.

Vacuum systems

During the course of this work three vacuum systems have been used to deposit metal exclusively for this program. These systems are a Sloan sputter deposition system with backsputter capability, a conventional

evaporation system using resistance heating, and a VEECO dual electron-beam evaporator with an AIRCO Temescal CV-14 power supply. The sputter system is pumped by a turbomolecular pump and will pump down to $\sim 2 \times 10^{-7}$ Torr in several hours. The system has ports for three magnetron sputter guns with cylindrical targets. Two sputter guns are in place while the third port is blanked off. When the substrate is sputter cleaned or sputter oxidized it is positioned under this third port. Niobium deposition rates of ~2,000 Å/min and critical temperatures close to that of bulk niobium for nominal thicknesses of 1,500 - 3,000 Å are achieved in this system. Pressures during sputter deposition or sputter cleaning are measured with an MKS Instruments model 220 capacitance manometer with digital readout over four decades: 0.0001 to 1 Torr. Power during sputter cleaning or oxidation is supplied by a 500 W Henry power supply.

The conventional evaporation system is used for evaporation of lead and lead-gold alloys. This system is pumped by an oil diffusion pump and is normally pumped to $\sim 2 \times 10^{-6}$ Torr before evaporation is begun.

The electron beam evaporator is pumped by an oil diffusion pump and will pump down to $\sim 2 \times 10^{-7}$ Torr. During evaporation of niobium, however, the pressure in this system will come up to $\sim 2 \times 10^{-6}$ Torr. A water-cooled sputter cathode on which a 3-inch diameter silicon wafer can be mounted is in place in this system. The sputter cathode is ~12 inches above the top of the melt. Evaporation rates up to 6,700 Å/min and critical temperatures close to that of bulk niobium for nominal thickness of 1,500 - 3,000 Å have been obtained in this system.

Masks for photolithography

Photolithographic masks for three levels of metallization have been made for this program. The three levels are the base electrode of the junctions, the counterelectrode, and a normal-metal resistive shunt. Chromium masks deposited on 4-inch x 4-inch pieces of glass were made so that 3-inch diameter silicon wafers could be used as substrates. Both positive and negative versions of each mask were made so that the patterns could be etched or lifted off. These masks contain junctions of the following sizes:

junctions without shunts:

number of junctions	dimensions
2	250 μm x 250 μm
2	5 μm x 5 μm
5	2.5 μm x 2.5 μm

junctions with shunts:

number of junctions	dimensions
2	5 μm x 5 μm
5	2.5 μm x 2.5 μm

The 2.5 μm and 5 μm junctions are in two parallel rows of seven junctions each. The junctions in each row are 0.5 mm apart, and the two rows are 5 mm apart. The 250 μm junctions are halfway between the rows of smaller junctions and are 6 mm apart. The junctions are connected in parallel electrically so that each junction can be tested separately without sending current through other junctions. This design is shown schematically in Figure 1. A test fixture with spring-loaded

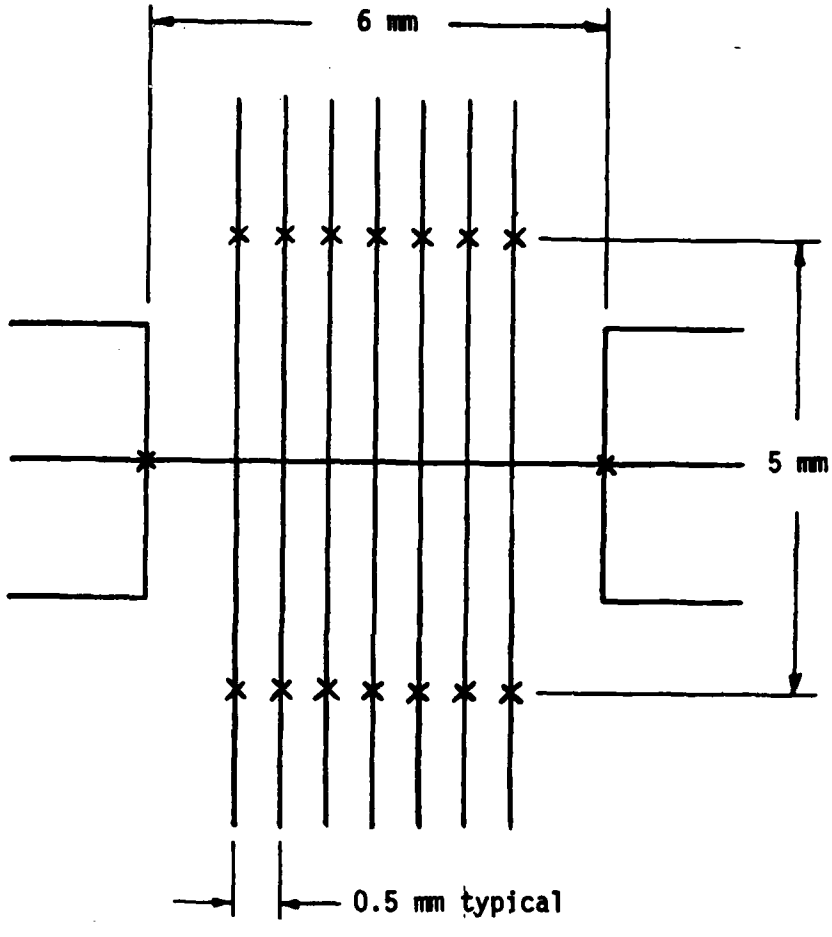


Figure 1. Schematic diagram of central part of photolithographic masks for junction fabrication.

probes was used to make electrical contact with pads on the substrates. This fixture was mounted on a probe which could be lowered into a liquid helium Dewar for testing.

Processing techniques

The niobium films that were made for this program were patterned in three different ways: by chemical etching, ion milling, and lift-off. The chemical etch that was used was as follows:

60 ml HNO_3
10 ml HF
100 ml H_2O

This etch worked well for linewidths of 5 μm or greater. Undercutting was a serious problem for smaller linewidths.

Ion milling worked quite well for all linewidths but was not ideal for films whose thickness varied across the substrate. In this case any lower levels of metallization would be partially milled away. This technique was the only one which could be used for the second level of Nb-Nb junctions, and problems with nonuniform layers of niobium were encountered.

Lift-off, using a 10-15 minute soak in chlorobenzene between exposure and development of the photoresist pattern to obtain an undercut stencil, worked quite well for sputtered niobium films. Linewidths as narrow as 2.5 μm were reproduced accurately. This method could not be used with e-beam evaporated niobium films because of excessive heating of the substrate during

evaporation. This occurred despite the fact that the substrates were heat sunk to a water-cooled plate.

Lead films were patterned by chemical etching and ion milling. Ion milling worked quite well for lead films because of the high milling rate for lead (compared to niobium). Unwanted milling of underlying niobium layers was kept to a minimum because of this high removal rate for lead. The chemical etch used for lead was the following:

10 ml acetic acid
10 ml HNO_3
100 ml glycerol

This etch worked fairly well, but sometimes over-etching occurred with films not uniform in thickness. Since patterning of the lead films was the final step in the fabrication of Nb-Pb junctions, it was especially risky to chemically etch them and they were usually ion milled.

Niobium-niobium oxide-lead junctions

During this program Nb-Pb junctions were made to learn the processing parameters for sputter cleaning and sputter oxidizing niobium base electrodes. Thermally oxidized Nb-Pb junctions were made to establish the sputter cleaning process. Once this process was determined, sputter oxidized Nb-Pb junctions

were made. A review of our results with Nb-Pb junctions is presented in this section.

All sputter cleaning and sputter oxidation was carried out in the Sloan sputter system using its backsputter capability. The parameters found to be best for sputter cleaning the niobium base electrode were:

rf power:	125 W
peak-peak rf voltage:	475 V
pressure:	0.005 Torr of Ar
time:	30 minutes

The parameters for sputter oxidation were:

rf power:	10 W
peak-peak rf voltage:	110 V
pressure:	0.005 Torr of Ar + 0.0002 Torr of O_2
time:	2 minutes

We consider the peak-peak rf voltage, rather than the rf power or power density, to be the important parameter for reproducing these processes since the rf voltage determines the energy of the ions impinging on the substrate. The rf power, however, was used to reproduce the plasma conditions from run to run and is therefore specified here and in what follows.

Parameters that were measured for each junction tested are:

maximum current at zero voltage, I_c

energy gap voltage, V_g, measured at the point of inflection of the current step in the single-particle I-V characteristic

current at 2 mV

current at 4 mV

From these measurements the following quantities were calculated:

$R_\ell = \frac{2\ mV}{I(2\ mV)}$ = resistance at 2 mV

$R_n = \frac{4\ mV}{I(4\ mV)}$ = resistance at 4 mV

R_ℓ/R_n

The quantity R_ℓ/R_n was used as a quality factor for the junctions.

The highest value of R_ℓ/R_n we obtained for sputter oxidized Nb-Pb junctions was 18. This particular junction was 5 μm x 5 μm and was a fairly high resistance junction with a low critical current. The other parameters for this junction were:

I_c = 0.4 μA
V_g = 2.9 mV
R_ℓ = 6.7 kΩ
R_n = 380 Ω

The I-V characteristic for this junction is shown in Figure 2.

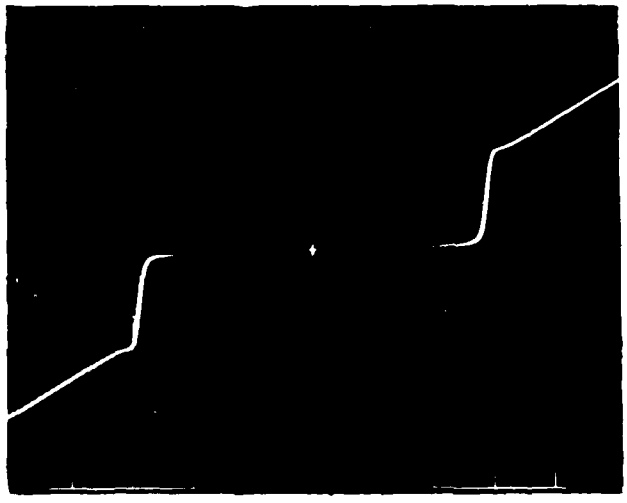


FIGURE 2. SPUTTER OXIDIZED Nb-Pb JUNCTION WITH $R_g/R_n = 18$

A parameter which IBM uses to characterize their junctions is V_m defined as:

$$V_m = I_c R_\ell$$

The highest value of V_m we have obtained for sputter oxidized Nb-Pb junctions was 12 mV. This particular junction was 25 μm x 25 μm. The other parameters for this junction were:

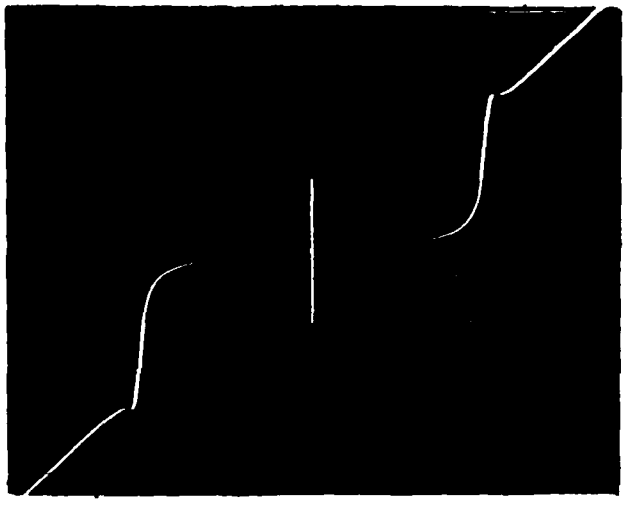
I_c = 240 μA
V_g = 2.9 mV
R_ℓ = 51 Ω
R_n = 6.0 Ω
R_ℓ/R_n = 8.6

The I-V characteristic for this junction is shown in Figure 3.

For comparison the best value of V_m we have obtained for a thermally oxidized Nb-Pb junction is 26 mV. This junction was 5 μm x 5 μm in size. The other parameters for this junction were:

I_c = 27 μA
V_g = 2.9 mV
R_ℓ = 960 Ω
R_n = 48 Ω
R_ℓ/R_n = 20

200 μA/cm



1 mV/cm

FIGURE 3. SPUTTER OXIDIZED Nb–Pb JUNCTION WITH $V_m = 12$ mV

The I-V characteristic for this junction is shown in Figure 4.

The values of V_m reported by IBM for Nb-Pb junctions range from 30-40 mV.[1]

Niobium-niobium oxide-niobium junctions

For the first experiments to fabricate Nb-Nb junctions the sputter cleaning procedure for the Nb-Pb junctions was used, and the sputter oxidation procedure for Nb-Pb junctions was used but for an extended time. IBM[1] has reported that for at least one set of oxidation conditions the oxidation time required to produce a given critical current density in Nb-Nb junctions is approximately five times as long as is required for Nb-Pb junctions. The first experiments to produce Nb-Nb junctions, therefore, were done under the following conditions:

sputter cleaning

rf power: 125 W
pressure: 0.005 Torr of Ar
time: 30 minutes

sputter oxidation

rf power: 10 W
pressure: 0.005 Torr of Ar + 0.0002 Torr of O_2
times: 5, 10, and 20 minutes

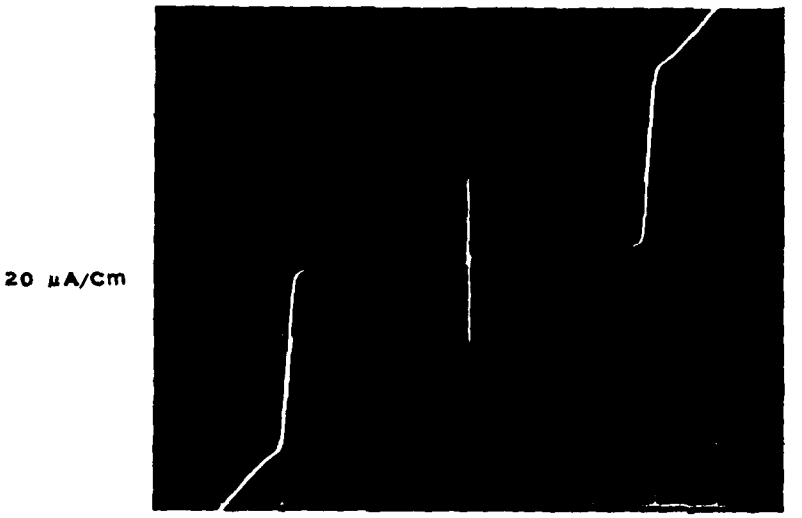


FIGURE 4. THERMALLY OXIDIZED Nb–Pb JUNCTION WITH $R_\ell/R_n = 20$ AND $V_m = 26\,mV$

counterelectrode

evaporated Nb (substrate not cooled during evaporation)

pattern ion milled

Although a 10-minute oxidation time was five times as long as the oxidation time required for Nb-Pb junctions under the same conditions, the I-V curves for these junctions showed no signs of an increase in current at the energy-gap voltage (which would indicate tunneling). The fact that the substrate temperature was allowed to rise during evaporation may have had a detrimental effect on the junctions.

IBM[2] has also shown that by increasing the total pressure during oxidation, but maintaining the same Ar/O_2 ratios, the oxidation times required for Nb-Nb junctions can be reduced to those for Nb-Pb junctions. The total pressure during oxidation reported by IBM was approximately 0.04 Torr. Our next experiments to produce Nb-Nb junctions used these higher pressures during oxidation:

sputter cleaning

rf power: 125 W

pressure: 0.005 Torr of Ar

time: 30 minutes

sputter oxidation

rf power: 10 W

pressure: 0.0385 Torr of Ar + 0.0015 Torr of O_2
(total pressure = 0.040 Torr)

times: 2, 5, 10, and 20 minutes

counterelectrode

evaporated Nb (substrate not cooled)

pattern ion milled

Again none of these junctions showed any signs of tunneling (as would be evidenced by a sudden increase in current at the energy-gap voltage).

For our next series of experiments it was decided to increase the amount of oxygen in the argon-oxygen mixture during sputter oxidation to increase the oxide thickness. The total pressure during sputter oxidation was kept at 0.040 Torr. The following conditions were used:

sputter cleaning

rf power: 125 W

pressure: 0.005 Torr of Ar

time: 30 minutes

sputter oxidation

rf power: 10 W

pressure: 0.0370 Torr of Ar + 0.0030 Torr of O_2

times: 5, 10, and 20 minutes

counterelectrode

evaporated Nb (substrate not cooled)

pattern *ion milled*

None of the junctions oxidized for 5 minutes showed any sudden increase of current at the energy-gap voltage. However, one of the large junctions (250 μm x 250 μm) on the substrate that was oxidized 10 minutes and both large junctions on the substrate that was oxidized 20 minutes showed a distinct increase of current at ~ 2.8 mV. (The second large junction on the substrate oxidized 10 minutes could not be measured because of problems with the spring probes making contact to that particular junction.) The best of these junctions was the one oxidized 10 minutes, and its I-V characteristic is shown in Figure 5. The following parameters were measured for this junction:

I_c = 40 μA

V_g = 2.8 mV

R_ℓ = 6.5 Ω

R_n = 4.3 Ω

R_ℓ/R_n = 1.5

V_m = 0.26 mV

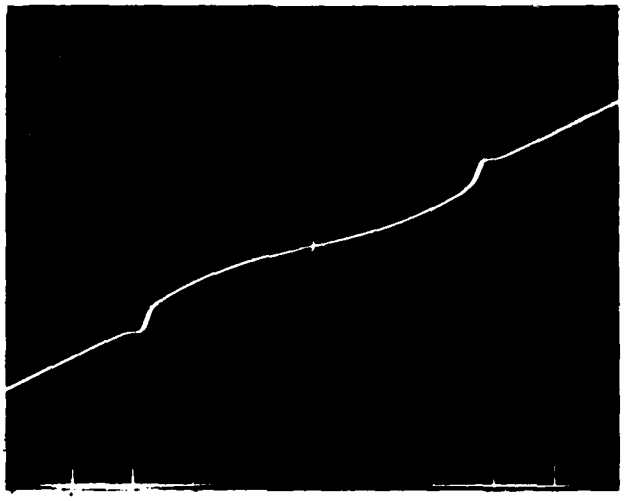


FIGURE 5. SPUTTER OXIDIZED Nb–Nb JUNCTION WITH $R_\ell/R_n = 1.5$ AND $V_m = 0.26$mV

Comparison can be made between the characteristics for this junction and Nb-Nb junctions made by IBM where no post-oxidation processing steps were done to improve the junctions. The range of values of V_m reported by IBM for such junctions is 3.0-3.5 mV.[2] By measuring the appropriate I-V characteristic in Figure 7 of this same reference, R_ℓ/R_n for these junctions is found to be 3.0, a factor of 2 greater than ours. This means that if the subgap current at 2 mV were reduced by a factor of 2 in our junctions, they would have the same subgap-to-normal state resistance ratio as those of IBM processed in a similar manner. The low value of critical current (and, therefore, low V_m) for our junction can be only partially accounted for by trapped flux. (The junction was large and cooled in the earth's field.) The critical current of a junction 250 μm square will be reduced by about 8% if it is cooled in the horizontal component of the earth's field.

It is interesting that only the largest junctions on these last two substrates showed any signs of tunneling. The smallest junctions on the substrates were 2.5 μm x 2.5 μm, a factor of 10^4 smaller in area than the large ones. One usually expects the smallest junctions to have the greatest chance of being good since the chance of having defects in the tunnel barrier should be smallest for these junctions. It seems that the only conclusion one can draw from our results is that perhaps there is leakage current at the edges of the junctions where the upper electrode crosses the base electrode. Edge effects should be minimal for large junctions since the ratio of edge length to junction area is smallest for large junctions. An experiment

to test this hypothesis would be to make "window" type junctions where the junction area is defined by an opening in an insulating layer.

Near the end of the contract period a fixture was obtained which enabled us to mount the substrate on a water-cooled plate in the e-beam evaporator. This fixture enabled us to keep the substrate cooler during evaporation of the niobium counterelectrode. Besides possible problems with the edges of the junctions, excessive heating during evaporation of the niobium counterelectrode may have caused the tunnel barrier to deteriorate. Additional substrates were processed identically to the one that had the best junction, with the exception that the new substrates were heat sunk to this water-cooled plate during the niobium evaporation. However, we were unable to duplicate our previous results with these substrates, and none of the junctions displayed tunneling I-V characteristics.

Another substrate was processed using the water-cooled substrate holder during evaporation of the niobium counterelectrode, but with double the oxygen-argon ratio during sputter oxidation (0.0340 Torr of Ar + 0.0060 Torr of O_2). The substrate was oxidized 10 minutes. None of the junctions on this substrate displayed tunneling I-V characteristics either.

Even though a water-cooled substrate holder was used during these last experiments, problems still remain. These are evidenced by the fact that the substrate was still getting too hot during evaporation of the niobium

counterelectrode for us to pattern it by lift-off. Several experiments were done to try to lift off evaporated niobium films, but in every case the photoresist had become baked on too well to allow it to be dissolved by acetone. If the niobium evaporation rate could be reduced by improving the vacuum in the system, substrate heating could be reduced and lift-off might become possible. Better junction I-V characteristics may also result from reduced substrate heating.

Niobium-aluminum oxide-aluminum-niobium junctions

Experiments were performed to make Nb-Nb junctions with aluminum-oxide barriers.[3] These junctions were made entirely with the sputter deposition system. The object of the experiments was to deposit less than 100 Å of Al on top of the niobium base electrode, oxidize the thin aluminum film, deposit a second thin aluminum film, and deposit the upper niobium electrode. Experiments were also done leaving out the second aluminum film, but the best results were obtained with it. Thicknesses of the aluminum films were adjusted by varying the deposition time at a constant power setting. Deposition times ranged from a few seconds to 20 seconds. Oxidation of the aluminum films was done thermally at room temperature in 1 Torr of oxygen. Junction characteristics were a function of oxidation time for times up to 2 hours. Device characteristics did not change for longer oxidation times. Parameters that were varied during these experiments were the thicknesses of the two aluminum films and the oxidation time. The best junction characteristics were obtained with 2 hour oxidation times.

The following procedure produced the best set of aluminum-oxide barrier junctions:

sputter cleaning of the Nb base-electrode surface

- rf power: 125 W
- pressure: 0.010 Torr of Ar
- time: 15 minutes

Al deposition

- current: 1 A
- voltage: 305 V
- pressure: 0.010 Torr of Ar
- time: 7 seconds

oxidation

- pressure: 1 Torr of O_2
- temperature: room temperature
- time: 2 hours

Al deposition

- current: 1 A
- voltage: 305 V
- pressure: 0.010 Torr of Ar
- time: 10 seconds

Nb deposition

- current: 4.0 A
- voltage: 325 V
- pressure: 0.020 Torr of Ar
- time: 70 seconds

All the preceding steps were accomplished in a single pump down. Patterning of both the lower and upper electrodes was done by lift-off.

Figure 6 shows the I-V characteristic for the best of these junctions. The following parameters were measured for this junction:

I_c = 1.5 μA

V_g = 2.4 mV

R_{subgap} = 571 Ω

R_n = 280 Ω

R_{subgap}/R_n = 2.0

V_m = 0.86

Summary and conclusions

The best results that were obtained for junctions made during this program are shown in Table 1. From the partially successful results that were obtained it appears that our processing procedure is close to one which would produce good Nb-Nb tunnel junctions. There are at least two important changes that can be made which should improve both the quality and reproducibility of the junctions we are making. One of these is to improve the vacuum in our e-beam evaporator so that the niobium can be deposited at a lower rate and, therefore, with less heat being dissipated in the system. A first step at improving the vacuum in the system is to add a Meissner trap in the vacuum chamber. This is being implemented and may reduce the pressure by a factor of 10. This would have the additional

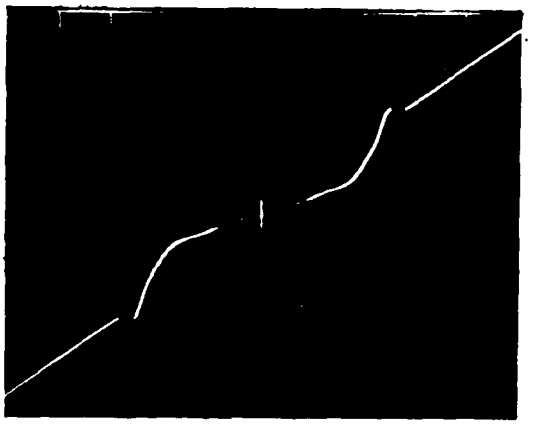


FIGURE 6. THERMALLY OXIDIZED Nb-Al OXIDE-Al-Nb JUNCTION

benefit that the reduced substrate temperature may enable the niobium counterelectrode to be lifted off rather than having to be ion milled. The junction fabrication procedure would be simplified, and variation in thickness of the niobium counterelectrode across the substrate would not be a problem.

Table 1

Summary of Results of Experiments
to Make Nb-Nb Tunnel Junctions

	best R_ℓ/R_n	best $V_m = I_C R_\ell$
Nb-Nb oxide-Pb		
thermally oxidized	20	26 mV
sputter oxidized	18	12 mV
Nb-Nb oxide-Nb		
sputter oxidized	1.5	0.26 mV
Nb-Al oxide-Al-Nb		
thermally oxidized	2.0	0.86 mV
IBM Nb-Nb oxide-Nb		
sputter oxidized; no post oxidation treatment	3.0	3.0 - 3.5 mV

The second change in the processing is to sputter clean, sputter oxidize, and evaporate the niobium counterelectrode all in the e-beam

evaporator without breaking vacuum. A water-cooled sputter cathode has been installed in the system, and an rf power supply and matching network are being connected to it.

Junctions are being made at the present time with aluminum barriers which have been sputter oxidized rather than thermally oxidized. In future experiments the aluminum-oxide barrier could be tried by sputtering the aluminum in a partial oxygen atmosphere. This may create a more uniform tunnel barrier and should enable thicker barriers to be made.

We have purchased a silicon target for our sputter deposition system so that we can also do experiments to make silicon barrier junctions. However the aluminum-oxide barrier junctions should be pursued further before trying a different barrier material.

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20. ABSTRACT

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