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Plasma nitridation process for the fabrication of all-refractory Josephson junctions

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A process for the fabrication of high-quality, all-refractory Josephson junctions of the type $Nb/Si_xN_y/Nb$ is described in detail. The junctions have been fabricated using the selective niobium anodization process with a tunnel barrier consisting of an amorphous Si film converted to its nitride by the application of a rf plasma of nitrogen. An attractive feature of these junctions is their comparably low specific capacitance $C/A = 3.9 \pm 0.1\ \mu F/cm^2$ (for $J_c = 6\ A/cm^2$). Junctions of this type having critical current densities up to $J_c = 2000\ A/cm^2$ and $V_m = 16$ mV have been fabricated. Excellent magnetic field threshold curves have also been observed for these junctions, indicating that the critical current density is very uniform.

I. INTRODUCTION

Thin films of Nb and NbN are widely used as electrodes for superconducting quantum interference devices (SQUIDs) because of their excellent mechanical strength and resilience to repeated thermal cycling. In most cases, the tunnel barriers used to fabricate the Josephson junctions have either been the native oxide or various deposited oxides. Due to the detrimental effect of oxygen on Nb, however, it is of interest to consider alternative nonoxide barriers. With the selective niobium anodization process (SNAP) reported by Kroger *et al.*[1] several years ago, thin films of amorphous Si were used as tunnel barriers. The resulting Josephson junctions had large subgap leakage currents, apparently due to the high density of localized states near E_F in the amorphous Si which provide alternate tunneling modes.[2,3] This detrimental feature was substantially reduced by using a triplelayer barrier having a region of hydrogenated amorphous Si in the middle.[4] In this report a simpler, alternative technique is described in which the barrier material of choice is converted to a nitride by the application of a rf plasma of nitrogen. Nitrides of silicon, for example, are widely used in the semiconductor industry and are very stable chemically. This latter feature makes the use of a nitride barrier with NbN electrodes very attractive.

Reactive sputter deposition of aluminum nitride barriers on NbN base electrodes has been reported previously.[5] These junctions had soft metal counterelectrodes and were of a reasonable quality. From this investigation using Nb electrodes, it was found that the formation of the nitride using a nitrogen plasma after the deposition of the starting barrier material provided better coverage. A similar technique has been used to fabricate junctions on VN films.[6] A high yield of good-quality junctions was reported; however, these junctions were also prepared using soft metal counterelectrodes. Our process using all refractory electrode materials should provide a more stringent test of the barrier technology. The fabrication process is described in detail in Sec. II, and the measurement results are described in Sec. III. A summary appears in Sec. IV.

II. FABRICATION PROCESS

All of the junctions studied in this investigation were fabricated in an oil diffusion pumped chamber equipped with three 10-cm-diam sputter targets. The chamber had a base pressure of typically 2×10^{-5} Pa. When throttled, the pressure rose to around 5×10^{-5} Pa and stabilized after about 1 min. The junctions were fabricated on 2-in.-diam polished silicon wafers having a thermally grown oxide about 0.5 μm thick. For deposition, the subtrate was thermally anchored to a copper substrate carrier using a very low-vapor-pressure diffusion pump oil. The use of oil rather than grease was found to be preferable because the oil could easily be washed away afterwards using alcohol. The carrier was then introduced into the deposition chamber via a load-lock mechanism and placed on a 23-cm-diam water-cooled substrate table. Diffusion pump oil was also used to improve the thermal contact at this interface.

All of the junctions were fabricated using SNAP. The individual layers were structured using either lift-off stencils or various wet etch techniques. The deposition modes and parameters are summarized in Table I.

The sputtered Nb films fabricated using this chamber proved to be of high quality. Films prepared using the conditions listed in Table I had a T_c of 9.1 K. Extremely narrow transition widths of 2 mK have been observed. The films had a resistivity ratio $R_{300}/R_{10} = 5.3$ and residual resistivity $\rho_{300} - \rho_{10} = 14.6\ \mu\Omega$ cm. The latter agrees with previous results reported for dc magnetron sputtered Nb thin films.[7] An x-ray analysis of the films indicates that they are preferentially oriented with the (110) axis perpendicular to the substrate and have a lattice constant $a = 3.329$ Å. This is slightly larger than the ASTM value for bulk Nb, indicating that the films are under compressive stress. It has been shown that Nb film stress may have an adverse effect on junction quality.[8] The sputter conditions for Nb are currently being studied in order to minimize this effect.

For device fabrication, first a trilayer was deposited over an entire wafer. The target-to-substrate distance was 70 mm for all depositions. The use of a smaller separation for the Si deposition was found to diminish the uniformity of the film thickness. The nitridation step was carried out immediately after the deposition of the Si layer. The chamber was first pumped to remove the argon, then throttled, and backfilled with nitrogen to 1.5 Pa. A rf plasma was then used to nitride the fresh amorphous Si film to form the tunneling barrier.

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TABLE I. Process conditions for junction fabrication.

Layer	Material	Mode	Pressure	Power	Rate	Thickness
base	Nb	dc magnetron	1.0 Pa Ar	12.2 W/cm^2	260 nm/min	300 nm
barrier	α-Si	rf magnetron	1.0 Pa Ar	0.49	1.1	2
nitridation	···	rf diode	1.5 Pa N_2	0.06[a]	(1 min)	···
counter	Nb	dc magnetron	1.0 Pa Ar	1.1	25	30
wiring	Nb	dc magnetron	1.0 Pa Ar	12.2	260	300

[a] The induced voltage on the substrate was reduced to 80 V by inserting a 5-kΩ resistor between the substrate table and ground.

The time was kept fixed at 1 min.

It was found that the trilayer could be most conveniently and quickly structured using a wet etch process. Although undercutting of 0.5–1 μm was observed, this was not critical for the gross definiton of the overall structure since the linewidth was rather large. The junction areas were next defined by protecting the desired contact areas with photoresist and then anodizing the remaining areas of the top Nb film. For device applications, additional large-area contacts to provide zero-voltage connections to the base electrode could also be defined during this step. This was followed by the deposition of a Nb interconnect layer. For our applications this film was most easily patterned using a lift-off process.

The fabrication process proved to be very quick; it was possible to easily complete a wafer in 1 day. A further savings in time could be gained by eliminating the initial wet etch step and relying on the anodic oxide to isolate the counterelectrode from the underlying base electrode. This proved satisfactory when spring-loaded pressure contacts were used for making electrical connections to the samples. For some measurements, however, it was necessary to make electrical connections using wire bonding. With this technique, the bond apparently pierced through the anodic oxide, as shorts were always produced. For this reason, most wafers were fabricated with the trilayer etch step included.

III. RESULTS

The I-V characteristic of a typical junction having a pure amorphous Si barrier measured at 4.2 K is shown in Fig. 1. The thickness of this barrier as determined from the calibrated sputter rate was 4.5 nm. The critical current is much lower than one would expect theoretically, and there is a substantial amount of leakage current. However, it was never necessary to oxidize the amorphous Si films in order to obtain reasonable tunneling characteristics. This indicates that the coverage of the Si films was good. When Si films of this thickness were exposed to a nitrogen plasma, the tunneling resistance at room temperature increased by a factor of around 200 000. In order to fabricate tunnel junctions having resistances of a few ohms it was necessary to reduce the starting amorphous Si thickness down to 2 nm.

The effects of the plasma power density and induced voltage on the wafer during the nitridation step are shown in Fig. 2. Plotted are the I-V characteristics for three junctions, each of which was fabricated using the same 2-nm initial amorphous Si thickness, but nitrided under different conditions. In order to reduce the apparently detrimental effect of the large induced voltage on the substrate during nitridation, a shunt resistor between the substrate table and ground was installed. For a power density of 0.12 W/cm^2 and a shunt resistance of 10 kΩ, the induced voltage was reduced to 120 V. The I-V characteristic of the third junction shown in Fig. 2 was fabricated in this way and had a sum gap equal to that which was obtained for junctions fabricated using pure amorphous Si barriers. The best junctions were obtained using a power density of 0.06 W/cm^2 and a shunt resistance of 5 kΩ to yield an induced voltage of 80 V. A typical I-V characteristic measured at 4.2 K for a junction fabricated in this way is shown in Fig. 3. This junction had a V_m ($=I_c R_{2\,\mathrm{mV}}$) value of 16 mV.

Although it was not possible to investigate the chemical composition of the nitrided barriers used in this study, the depth to which nitrogen can be incorporated in a Si film was inferred from an Auger depth profile analysis. The sample used consisted of a 30-nm-thick amorphous Si film deposited onto a Nb-coated wafer and then heavily nitrided in a 1.5-Pa nitrogen plasma with a power density of 0.24 W/cm^2 and induced voltage of 380 V for 5 min. The power density and induced voltage were the same as had been used to fabricate the junction having I-V characteristic No. 1 in Fig. 2. Additional samples for determination of the etch rate during nitridation were also prepared by nitriding for 30 min. From film thickness measurements using a step profilometer, it was inferred that approximately 3 nm of Si was etched away

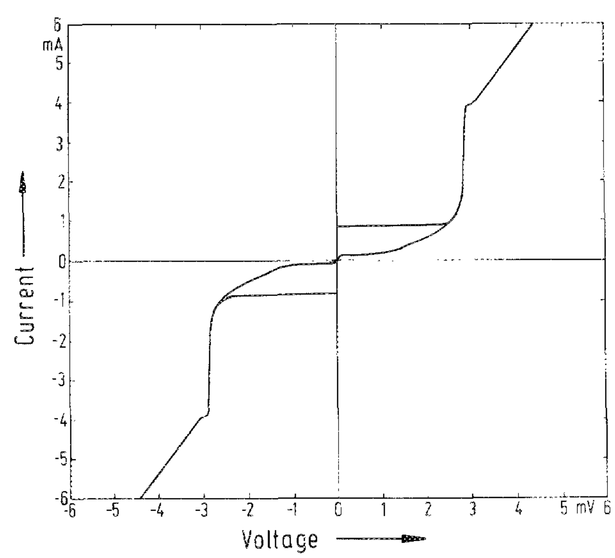

FIG. 1. I-V characteristic of a typical junction having a pure amorphous silicon barrier measured at 4.2 K.

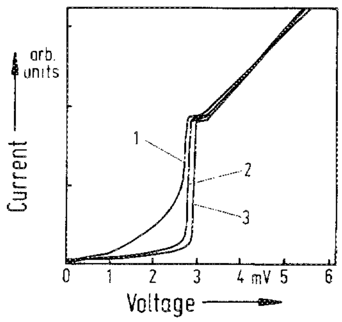

FIG. 2. *I-V* characteristics of three junctions fabricated using a nitrogen plasma power density and induced voltage at the wafer, respectively, of (1) 0.24 W/cm^2, 380 V, (2) 0.12 W/cm^2, 240 V, and (3) 0.12 W/cm^2, 110 V (reduced by inserting a 10-kΩ resistor between the sample holder and ground). The Josephson currents have not been shown for clarity.

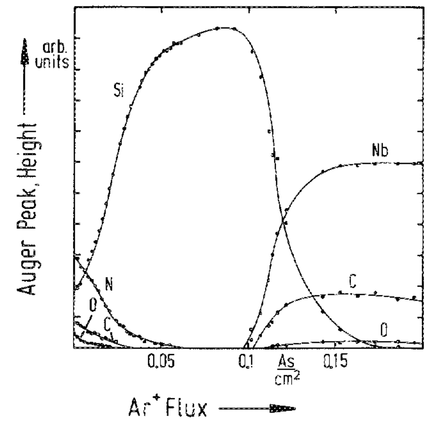

FIG. 4. Auger depth profile of a 30-nm amorphous Si film deposited onto a Nb-coated substrate and subsequently nitrided in 1.5 Pa of N using a rf power density of 0.24 W/cm^2 and induced voltage of 380 V for 5 min.

during nitridation under the conditions used to prepare the Auger sample. Films nitrided under the same conditions used to form the tunneling barriers, however, showed no measurable change in the Si thickness to within the precision of the measurement, estimated to be 10%.

The measured Auger peak heights versus Ar-ion beam flux for the Auger sample are shown in Fig. 4. If one assumes that the etch rates for Si and nitrided silicon are comparable, one may then use the length scale obtained from the time required to etch through the remaining 27-nm-thick nitrided Si film to infer that the nitrogen has penetrated to a depth of around 12 nm. This is much greater than the 2-nm thickness of Si that was used for barrier fabrication and probably accounts for the substantial degradation of the *I-V* characteristic for junction No. 1 shown in Fig. 2; that is, N has most likely gone through the 2 nm Si layer and penetrated the underlying Nb electrode. The significant improvement observed in the *I-V* characteristics Nos. 2 and 3 in Fig. 2 obtained by reducing the power density and induced voltage during nitridation is probably due to a decrease in the depth to which N penetrates the Si/Nb bilayer. A further reduction of the power density or induced voltage much below the optimum values of 0.06 W/cm^2 and 80 V, respectively, resulted in junctions exhibiting microshorts, while junctions

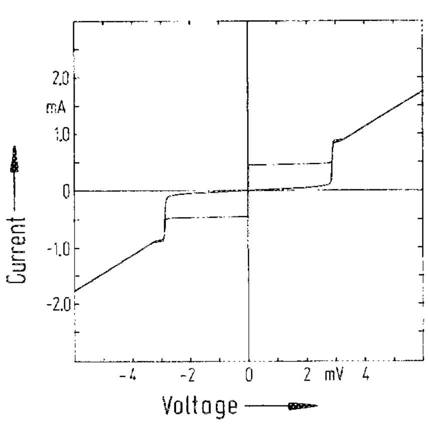

FIG. 3. *I-V* characteristic of a 25 μm $\times$ 25 μm junction having a nitrided silicon barrier measured at 4.2 K. For this junction, $V_m = 16$ mV and $I_c R_n = 1.48$ mV.

fabricated without the nitridation step altogether were shorts. Thus it is believed that the optimal nitridation conditions were sufficient to nitride most, if not all, of the 2-nm Si layer with little N penetration into the underlying Nb electrode. More exact information about the stoichiometry and extent of the nitrided region could be inferred from an XPS analysis of the nitrided Si/Nb bilayers. It is known from XPS studies of silicon nitride films[9] that the Si 2*p* core level shift gives a measure of the nitrogen concentration in the film. Such an analysis would need to be carried out *in situ* and was not possible for this investigation.

The magnetic field dependence of the maximum Josephson current for junctions fabricated using this technique has been investigated. The measurements for one such junction are shown in Fig. 5. It was found that the maximum Josephson current vanished at most of the minima, indicating that the Josephson current density is very uniform. Using the Nb penetration depth as the single adjustable parameter, excellent agreement was obtained with the theoretical prediction for $\lambda = 73.4$ nm. This compares very favorably with the value of 76.5 nm reported for electron-beam-deposited Nb films,[10] less so with the values of 120,[11] 86,[12] and 40 nm[13] reported for dc magnetron sputtered films. The reason for the large spread in λ reported for the dc magnetron films is not clear.

The *I-V* characteristics of the junctions used for the above measurements also exhibited a number of Fiske steps with applied magnetic field. The width of the voltage steps and the value of the Nb penetration depth derived previously were used to calculate the specific capacitance C/A, yielding 3.9 ± 0.1 and $4.6 \pm 0.5\ \mu$F/cm^2 for junctions having critical current densities J_c of approximately 6 and 60 A/cm^2, respectively. The reduced barrier thicknesses $t/\epsilon = \epsilon_0 (C/A)^{-1}$ are 2.28 and 1.93 nm. From the known sputter rate, the corresponding barrier thicknesses t of 2.6 and 2.07 nm were used to calculate the dielectric constant ϵ of the nitrided silicon layer, yielding 11.4 and 10.7, respectively. This is to be compared with a value of 7.1 reported for pure Si_3N_4 films.[14] The rather large discrepancy for ϵ may be due to the uncertainty in precisely determining the barrier thick-

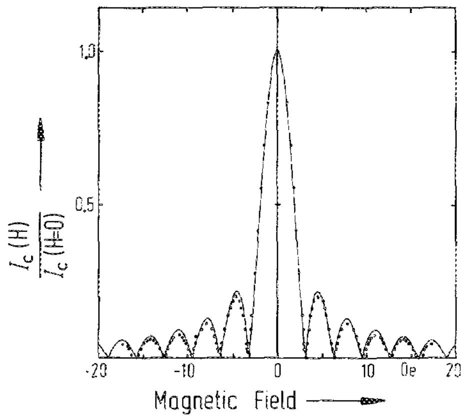

FIG. 5. Magnetic field dependence of the maximum Josephson current for a 44 μm $\times$ 44 μm junction.

ness or an indication that the nitrided Si films are nonstoichiometric.

A rough estimate of the specific capacitance of the nitrided silicon barrier junctions was also derived from another set of measurements in which the onset of hysteresis was observed for several junctions shunted with thin copper films which were slowly oxidized by repeatedly cycling the samples between room temperature and 4 K. The I-V characteristics for one set of measurements are shown in Fig. 6. The shunt resistance corresponding to the onset of hysteresis in the junction I-V characteristic, determined by the first observation of switching, was used to calculate the junction capacitance from the definition of the McCumber parameter.[15] This analysis assumes, of course, that the effects of noise are minimal, since the presence of noise increases the range of β_c over which the junction characteristics remain hysteretic. The effect of noise on junction I-V characteristics has been studied theoretically by Voss.[16] It was found that, for an effective noise strength parameter $\Gamma = 2\pi kT/I_c\Phi_0 = 0.01$, only slight rounding of the I-V characteristic occurs. Since Γ for the junctions used for the above measurements was in the range $0.01 \leqslant \Gamma \leqslant 0.02$, it is clear that the critical value for β_c is somewhat larger than the $T = 0$ value of 0.87. Using $\beta_c = 1$ as a rough estimate,

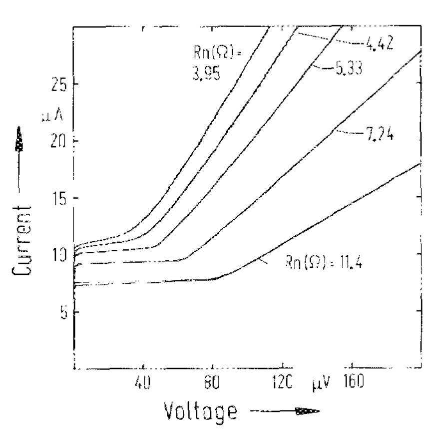

FIG. 6. I-V characteristics of a single, 4 μm $\times$ 4 μm junction for several different values of the Cu shunt resistance R. The resistance corresponding to the onset of hysteresis (here 7.24 Ω) was used with $\beta_c = 1$ to calculate the specific capacitance.

the measurements from five junctions having J_c of about 70 A/cm^2 yielded a specific capacitance of 4.5 ± 0.3 μF/cm^2, in surprisingly good agreement with the previous result.

The specific capacitance of the nitrided Si barriers is substantially lower than the value of 12 μF/cm^2 ($J_c = 100$ A/cm^2) reported by Magerlein[17] for Nb_2O_5 barriers and more than 30% lower than the values of 6 μF/cm^2 ($J_c = 600$–1300 A/cm^2) reported by Gurvitch, Washington, and Higgins[11] and 7 μF/cm^2 (J_c not specified) reported by Morohashi and Hasuo[18] for oxidized Al barriers, although in the latter two studies higher values of J_c have been used. For comparable J_c the difference in specific capacitance for nitrided Si and oxidized Al barriers is most likely somewhat smaller. Junctions fabricated using pure amorphous Si barriers have been reported[19] to have the lowest specific capacitance, only 2.5 μF/cm^2, but the high leakage current typically observed for these junctions (cf. Fig. 1) makes them less suitable for many device applications. It has been demonstrated[4] that this undesirable feature can be substantially reduced by using a triple-layer barrier having a region of hydrogenated amorphous silicon in the middle. Although the specific capacitance of these junctions was not reported, the lower dielectric constant of hydrogenated amorphous silicon and the observation that hydrogenated, triple-layer barriers and pure amorphous Si barriers of the same total thickness yielded junctions having comparable tunneling resistances above the energy gap suggests that the specific capacitance of hydrogenated, triple-layer barriers should be comparable to or possibly less than that for pure amorphous Si barriers. However, it was also observed[4] that the Nb electrodes were sensitive to H contamination, which can depress the Nb T_c, making adequate protection of the electrode surfaces essential. For the barrier technology described here, this does not seem to be the case with N. Thus the nitrided barriers provide a simple alternative to the hydrogenated, triple-layer barriers, at the expense of a somewhat larger junction capacitance.

An estimate of the nitrided Si barrier height was determined by fitting the junction I-V characteristics at high bias to the Simmons model.[20] This model predicts ohmic behavior for bias voltages less than the rectangular barrier potential ϕ_0/e. This was observed to be the case for bias voltages out to nearly 100 mV. For larger bias voltages it is not clear if the small deviations observed are real or due to heating effects associated with the rather large current required to carry out the measurements. From a fit to the data, a mean barrier height $\bar{\phi} = 0.45$ eV and a barrier thickness $s = 2.05$ nm was obtained. The barrier height is considerably higher than the values of 27 (Ref. 21) and 20 meV (Ref. 2) reported for sputtered and evaporated pure amorphous Si barriers, respectively.

We are currently using this junction technology to develop integrated dc SQUID magnetometers for biomagnetic measurement applications Recent results have been reported elsewhere.[22,23]

IV. SUMMARY

A process has been described for the fabrication of

Nb/Si_xN_y/Nb Josephson junctions. The junctions were fabricated using SNAP with the barrier formed by exposing a thin amorphous Si film to a nitrogen plasma. The formation of the nitride on the wafer after deposition of the Si film seemed to provide better coverage than films deposited reactively. Interfacial damage during the nitridation step was reduced by inserting a shunt resistor between the sample and ground so as to decrease the induced voltage at the wafer.

Junctions fabricated using this technique have proved to be rugged and reliable. Test junctions have been repeatedly cycled between room temperature and 4 K, and stored for over 1 year with no observable changes in their I-V characteristics. Values for V_m up to 16 mV have been obtained and excellent magnetic field threshold curves have been measured, indicating that the critical current density is very uniform. An attractive feature of these junctions is their comparably low specific capacitance, approximately 4 μF/cm^2 for $J_c = 6$ A/cm^2.

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