Modification of aluminum thin films

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We have utilized several processing techniques to locally modify the superconducting transition temperature and the normal state resistivity of aluminum thin films. The techniques of ion implantation, application of a magnetic overlayer, and reactive ion etching have been used to fabricate S-N interfaces with controlled differences in transition temperatures and normal state resistances. Lithographic techniques and CF_4 reactive ion etching at low power and pressure reliably produce two-dimensional S-N structures of desired dimensions in the limit where the transition temperatures and normal state electronic properties of the two regions are close to each other. *© 1995 American Vacuum Society.*

I. INTRODUCTION

Previous work[1] has shown that CHF_3/O_2 reactive ion etching (RIE) of aluminum thin films, combined with photolithography, produces well defined superconducting-normal metal (S-N) interfaces by selectively altering the superconducting transition temperature (T_C) of the films. We use normal metal to refer to a superconducting metal at temperatures above T_C. The etching process results in depression of the T_C by replacing the surface oxygen with fluorine. This RIE technique has been used to fabricate two-dimensional (2D) aluminum structures with periodically alternating T_C's and single S-N-S junctions. These structures are unique in that the modification is mainly at the surface, leaving the normal state electronic properties similar in both the altered and unaltered regions, and the T_C's of the two regions are close to each other. Some very interesting results, such as a proximity effect at long length scales[2] and an interfacial resistance increase,[3] have been reported in such fabricated structures. However, the underlying physics of these effects is not fully understood, and there is a need for further theoretical work. Motivated by the previous results and by the possibility of studying new S-N structures[4,5] or superconducting weak links,[6] we have developed efficient fabrication techniques to produce continuous aluminum film structures with different local T_C's and normal state resistances (R_N) in a controlled and systematic manner. These structures, with well defined dimensions, enable us to gain a better understanding of superconductivity in S-N metal films in the unexplored limit where the electronic transport properties (such as R_N) and the T_C's of two regions are close to each other.

II. BASIC SAMPLE FABRICATION

Aluminum thin film structures are defined on a substrate by photolithography followed by metal deposition and lift-off processing. The substrate is an ~1500-Å-thick insulating layer of silicon nitride deposited onto a silicon wafer by a LPCVD (low pressure chemical vapor deposition). Aluminum is evaporated either thermally or by electron beam heating onto a substrate held at room temperature. The deposition is performed in a base vacuum of $\sim 5\times10^{-7}$ Torr at a rate of ~15 Å/s using a CVC SC4500 evaporation system. The nominal thicknesses of the films are in the range 250–550 Å. Their diffusion constants, resistivities, and RRR's (residual resistance ratios) are 60–90 cm^2/s, 2–3 $\mu\Omega\,\mathrm{cm}$ and 2–3, respectively.

Next, a second layer of photolithography is used to define the regions where the aluminum film is to be modified, altering the T_C and R_N. Before producing this second layer, a thin coat (300–600 Å thick) of polymethylmethacrylate (PMMA) is first spun over the aluminum film and baked at 170 °C for 1 h as a protective layer against the metallic hydroxide photoresist developer. The developer would etch away the aluminum film if the film were not protected. The photoresist is then spun on the protected aluminum film. Both layers of photolithography are performed using a GCA DSW4800 10:1 stepper. After the development of the exposed area of photoresist, the thin protective PMMA layer can be removed safely by a dry etching technique. Since the selectivity of most etchants for PMMA against photoresist is relatively poor, a very thin layer of PMMA is desirable in order to ensure durability of the photoresist layer which will act as a mask against the subsequent modification of the aluminum film (see Fig. 1). The etching process for the PMMA must be performed carefully because there is a possibility of modification of the properties of the aluminum film by this processing step in addition to the main modification which follows. With this possibility in mind, the etching gas and parameters for PMMA should be chosen such that the desired total modification is still obtained (the actual parameters are given in Sec. III).

After the PMMA etching, the T_C and R_N of the resist free regions of aluminum films can be modified by either ion implantation, the addition of a magnetic overlayer, or RIE techniques. These modification techniques rely on different mechanisms to cause the T_C shifts. Finally, after the specific technique is implemented, the photoresist/PMMA layer is stripped by a wet etching technique in a solution of acetone and methylene chloride. No annealing of the aluminum films is done after any of these modification procedures. Some examples of possible final structures are shown in Fig. 1. The low temperature resistance measurements of these modified aluminum structures are carried out in a ^{4}He cryostat. In the

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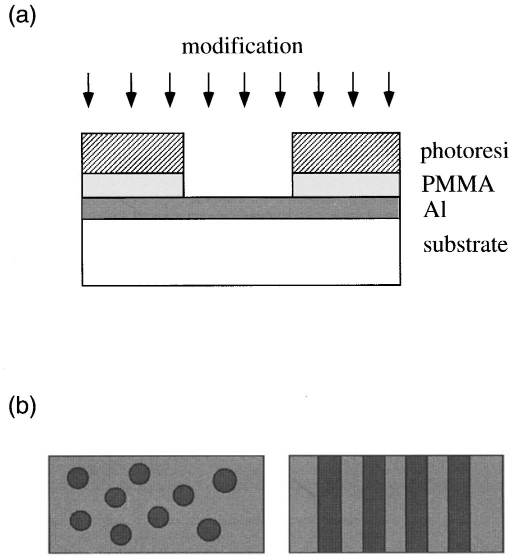

FIG. 1. Schematics of several sample configurations. (a) A cross section of the sample during modification. (b) Examples of possible final structures – superconducting islands and a 2D analog of a superlattice.

following sections we describe in detail the methods we use to modify the aluminum films.

III. TECHNIQUES TO MODIFY PROPERTIES OF ALUMINUM THIN FILMS

A. Ion implantation

One of the methods we have used to modify aluminum films is ion implantation. Before ion implantation, the protective PMMA layer is removed by a low power oxygen RIE (2 mTorr, ~50mW/cm^2, 30 sccm, ~3 min). The T_C and R_N changes due to this removal are small compared to those of ion implantation (for details see Sec. III C on oxygen RIE). We use an Accelerators Inc. 300R implanter, and the changes in the T_C and R_N of aluminum films are controlled by varying ion species and implantation doses. We have used oxygen and fluorine ions with doses equivalent to one to five monolayers at 5 keV. A low accelerating voltage is chosen in order to ensure that most of the ions will be stopped in the aluminum films which have a thickness of a few hundred angstroms. The mean ranges and lateral straggling lengths of implanted oxygen and fluorine ions, predicted by a computer simulation,[7] are 120–140 and 60–70 Å, respectively. We expect that most of the ions to be implanted within our films and the sharpness of the interface between the implanted and adjacent unimplanted regions to be ~100 Å. The corresponding projected mean ranges in photoresist are 200–300 Å, hence 1–2 μm-thick resist is sufficient to protect other regions of the aluminum films from inadvertent ion implantation.

In Fig. 2, the electronic resistance of such implanted aluminum films is plotted against temperature. The implantation results in positive T_C shifts and large increases in R_N, proportional to ion dose, mainly due to structural damage caused by the energetic ions which are deposited throughout the entire volume of the film. The effect of oxygen ion implantation on the film is much stronger than that of fluorine.

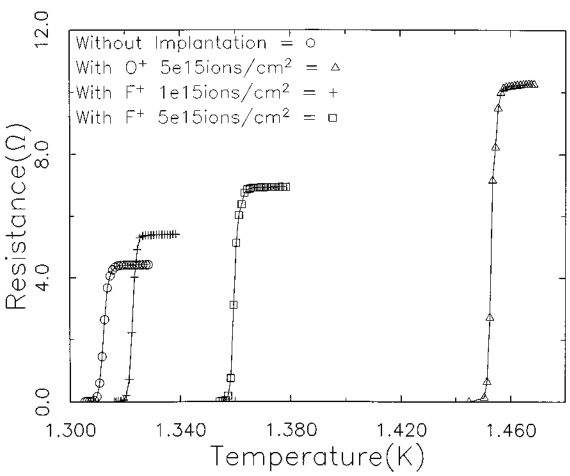

FIG. 2. T_C shifts due to oxygen and fluorine ion implantations. Note the change in resistance after implantation.

An oxygen implantation at a dose of 5×10^{15}ions/cm^2 increases the T_C by 11% and the normal state resistivity by 130%, and decreases the diffusion constant by 53% and the RRR by 34%, whereas a fluorine implantation at the same dose increases the T_C by 4% and the normal state resistivity by 57%, and decreases the diffusion constant by 35% and the RRR by 21% (see Table I).

Ion implantation techniques provide an efficient way to systematically fabricate S-N or S-I (superconductor-insulator) interfaces. Many papers have reported the use of ion beam irradiation (implantation, milling, or sputtering) as a method of altering the electrical behavior of superconducting materials[8–10] and patterning them,[11,12] and ion beam irradiation has been applied to high-T_C superconducting device fabrication.[13,14] However, this method is unsuited for our purpose of fabricating S-N structures where the T_C's and electronic transport properties of two regions have to be close to each other because it causes a large change in the electrical characteristics of the modified region. Another drawback of this technique occurs during processing. When the regions of modification are patterned on the metal film by photolithography (or electron beam lithography), the phororesist (or PMMA) layer is used as a mask against the ion implantation. Hardening of the resist occurs at the side

TABLE I. Low temperature electronic transport properties before and after ion implantation of the aluminum films whose resistive transitions are shown in Fig. 2 [superconducting transition temperature (T_C), residual resistance ratio (RRR), normal state resistivity (ρ_n), normal state sheet resistance (R_S), and mean free path (l)].

		F$^+$ implantation		O$^+$ implantation
	Before implantation	1×10^{15} ions/cm^2	5×10^{15} ions/cm^2	5×10^{15} ions/cm^2
T_C (K)	1.312	1.323	1.360	1.453
RRR	2.8	2.5	2.2	1.9
ρ_n ($\mu\Omega$ cm)	1.5	1.9	2.4	3.6
R_s (Ω)	0.28	0.36	0.45	0.68
l (Å)	139	126	90	66

walls because the resist (which is hydrogen deficient from the radiation during ion implantation) becomes crosslinked and diamond-like.[15] The subsequent wet etching, even with ultrasonication, sometimes does not remove all the resist. The resist residue potentially causes stress in the aluminum film as the sample is cooled. If the removal of the residual resist by dry etching is attempted, unintended additional inhomogeneities in the film are unavoidable due to the material modification caused during the dry etching process.

B. Magnetic overlayer

Another method used to affect local T_C in a film is by the addition of a magnetic overlayer. First, the PMMA layer is removed by a low power oxygen RIE, as in the case of ion implantation, then a magnetic overlayer is deposited onto the aluminum film surface. Chromium is thermally evaporated at a rate of a few angstroms per second. We have performed low temperature resistance measurements on samples with chromium overlayers of thickness in the range of 10–30 Å. It is well known that T_C is suppressed in superconducting metal films in the presence of magnetic impurities due to the pair breaking mechanism.[16,17] The pair breaking parameter which represents the relative T_C shift[18] is empirically found to depend linearly on the normal state sheet resistance, with the zero resistance intercept and the slope strongly dependent on material and on sample preparation methods. In the aluminum film samples prepared in our laboratory with chromium overlayers, the shift in T_C is $\sim$10 mK or smaller. Deposition of chromium of thickness above 10 Å has little or no effect on the magnitude of the T_C shift, as in the case of Spahn *et al.*,[16] since in this range of thickness the magnetic overlayer covers the film surface completely. Even if a controlled T_C shift is possible with thinner overlayers (formed by slower evaporation rate), the maximum shift ($\sim$10 mK) is too small to reliably produce S-N structures when competing with the T_C shift from other processing related minor effects such as the shift from the O_2 RIE of PMMA. If one can prepare samples with a larger pair breaking parameter (as in the case of the quench condensed aluminum films of Spahn *et al.*), this magnetic overlayer T_C modification technique has the advantages of simplicity of patterning and production of a S-N interface with very similar normal state resistances.

C. Reactive ion etching

We have also tried to modify the T_C of aluminum film by the use of the O_2 or CF_4 RIE technique. In the case of RIE, the same gas is used to first remove the protective PMMA layer before the actual modification of the aluminum. An Applied Materials reactive etcher is used with either O_2 or CF_4 gas at a pressure of 2 mTorr. O_2 RIE is done at a power density of $\sim$50 mW/cm^2 with a flow rate of 30 sccm, and CF_4 RIE at $\sim$80 mW/cm^2 with 10 sccm. These plasma conditions are at a significantly lower power than the previous experiments.[1–3] These etching gases and parameters were chosen in order to noninvasively modify the aluminum film surface at a slow rate (for a better control of T_C shift) without causing any significant thickness reduction. Since both O_2 and CF_4 gases are very poor etchants of aluminum, the actual material removal by reactive ion etching with these gases at the above low powers and pressures is negligible. A low pressure also provides a straight etching profile and hence ensures a sharp interface between the modified and unmodified sections.

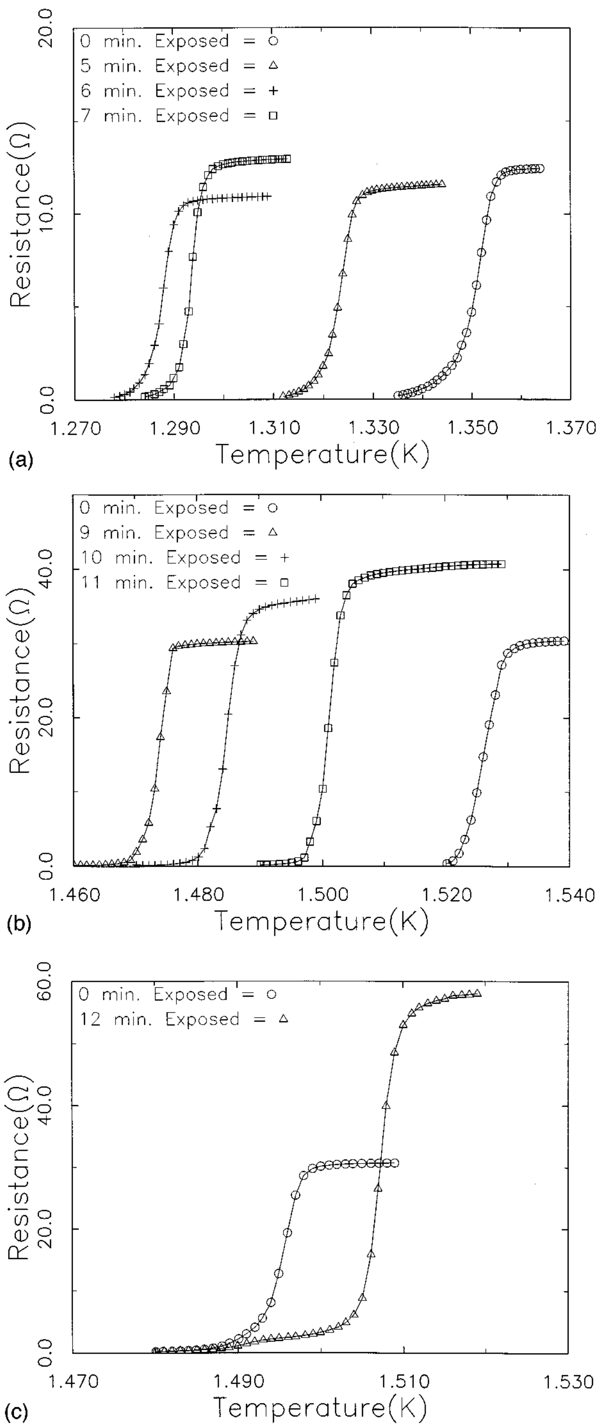

FIG. 3. T_C shifts due to CF_4 RIE. (a), (b) and (c) are data from three different aluminum samples. (a) shows the resistance decrease that accompanies the initial exposure of the film to the CF_4 RIE. The longest of these (7 min. □) shows an increase in T_C and resistance. (b) shows the systematic increase in T_C and resistance achieved by longer exposure times. (c) shows the final T_C exceeding that of the unexposed sample.

TABLE II. Low temperature electronic transport properties before and after CF_4 RIE of the aluminum films whose resistive transitions are shown in Fig. 3(a) [superconducting transition temperature (T_C), residual resistance ratio (RRR), normal state resistivity (ρ_n), normal state sheet resistance (R_S), and mean free path (l)].

	Before	CF_4 RIE		
	CF_4 RIE	5 min	6 min	7 min
T_C (K)	1.351	1.324	1.288	1.294
RRR	2.2	2.3	2.3	2.3
ρ_n ($\mu\Omega$ cm)	2.8	2.7	2.5	3.0
R_S (Ω)	0.80	0.77	0.71	0.86
l (Å)	162	145	142	134

Figure 3 shows the T_C shifts due to CF_4 RIE with different etching times. This technique produces negative T_C shifts, proportional to the etching time at first (once the PMMA layer is removed), but saturating with longer times. The negative T_C shifts are caused by the replacement of surface oxygen with fluorine.[1] When the film is exposed to the plasma over a long period of time, the secondary effect due to damage and surface erosion is no longer negligible and the negative T_C reverses, accompanied by a sudden increase in the normal state resistance [Figs. 3(a), 3(b)]. With even longer etching times, one can obtain a positive T_C shift with a large increase in the normal state resistance [Fig. 3(c)]. We have obtained T_C shifts of as much as 5%. The usual changes in normal state resistivity, diffusion constant, and RRR before or close to the saturation are $\sim$6%, $\sim$20%, and $\sim$1%, respectively (see Table II). The sharpness of the boundaries between the RIE modified and unmodified regions appear to be defined to 0.1 μm or better.[1]

This modification technique produces a S-N interface with well controlled T_C and R_N. It also provides the flexibility of fabricating S-N structures with either similar R_N's or different R_N's. By varying etching time, a desired magnitude of T_C shift, either a negative (as much as $\sim$60 mK) or positive, can be obtained. (The previous experiment[1] could not reliably predict ΔT_C.) In particular, this technique reliably produces S-N structures in the limit where the T_C's and R_N's of two regions are close to each other.

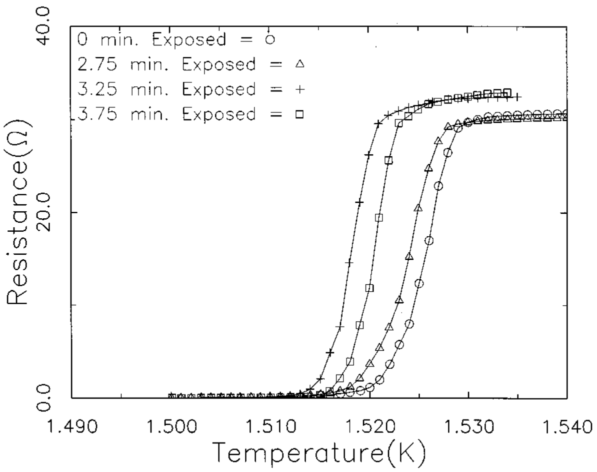

FIG. 4. T_C shifts due to O_2 RIE. These demonstrates the very small T_C shifts achieved with this technique.

Figure 4 shows the T_C shifts due to O_2 RIE which are similar to the effect of CF_4 RIE, but with a smaller range of ΔT_C. The maximum T_C shift obtained is only $\sim$10 mK. The surface modification with oxygen RIE at a low power has a small effect since there is native oxide layer on both the modified and unmodified regions. Although this method is not suited to actually fabricate S-N structures, given these small T_C shifts, this technique can be used to remove the protective PMMA layer before other major T_C modification techniques such as ion implantation and magnetic overlayer, and thus avoid an unintended modification during the processing.

IV. CONCLUSION

We have discussed various processing techniques to alter the superconducting properties of aluminum thin films. The CF_4 RIE technique, combined with photolithography, provides well defined S-N interfaces with controllable difference in the T_C's and R_N's of the two regions by local surface modification. Either negative or positive T_C shifts, and increases in R_N of desired magnitude, can be obtained by variation of RIE exposure time. This technique reliably produces S-N structures in the region where the T_C's and R_N's of both sides are close to each other. In contrast, ion implantation effectively shifts T_C, but with a large increase in R_N due to structural damage throughout the volume of the film. It is difficult to produce S-N structures with similar R_N's. However, this technique is effective when used to fabricate structures with substantial material alteration (for example, it can be used to simulate a conventional superlattice in 2D). Finally, the magnitude of the T_C shift induced by addition of a magnetic overlayer (on aluminum films evaporated at room temperature) is too small to realize actual S-N interfaces, but its potential application for use in the modification of quench condensed films is promising.

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