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 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 or superconducting weak links,$^4$ 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 $\approx$ 1500-Å-thick insulating layer of silicon nitride deposited onto a silicon wafer by 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 $\approx 5 \times 10^{-7}$ Torr at a rate of $\approx 15$ 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 $\mu$Ω 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
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/cm², 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, 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.

<table>
<thead>
<tr>
<th>Ion Implantation</th>
<th>Before Implantation</th>
<th>$1 \times 10^{15}$ ions/cm²</th>
<th>$5 \times 10^{15}$ ions/cm²</th>
<th>$5 \times 10^{15}$ ions/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_C$ (K)</td>
<td>1.312</td>
<td>1.323</td>
<td>1.360</td>
<td>1.453</td>
</tr>
<tr>
<td>RRR</td>
<td>2.8</td>
<td>2.5</td>
<td>2.2</td>
<td>1.9</td>
</tr>
<tr>
<td>$\rho_s$ (μΩ·cm)</td>
<td>1.5</td>
<td>1.9</td>
<td>2.4</td>
<td>3.6</td>
</tr>
<tr>
<td>$R_s$ (Ω)</td>
<td>0.28</td>
<td>0.36</td>
<td>0.45</td>
<td>0.68</td>
</tr>
<tr>
<td>$l$ (Å)</td>
<td>139</td>
<td>126</td>
<td>90</td>
<td>66</td>
</tr>
</tbody>
</table>

An oxygen implantation at a dose of $5 \times 10^{15}$ ions/cm² 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 and patterning them, and ion beam irradiation has been applied to high-$T_C$ superconducting device fabrication. 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
walls because the resist (which is hydrogen deficient from the radiation during ion implantation) becomes crosslinked and diamond-like. 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. The pair breaking parameter which represents the relative \( T_C \) shift 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. 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. \( \square \)) 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.
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. 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 $\mu$m or better.

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 could not reliably predict $\Delta T_C$.) 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.

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 $\Delta T_C$. 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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