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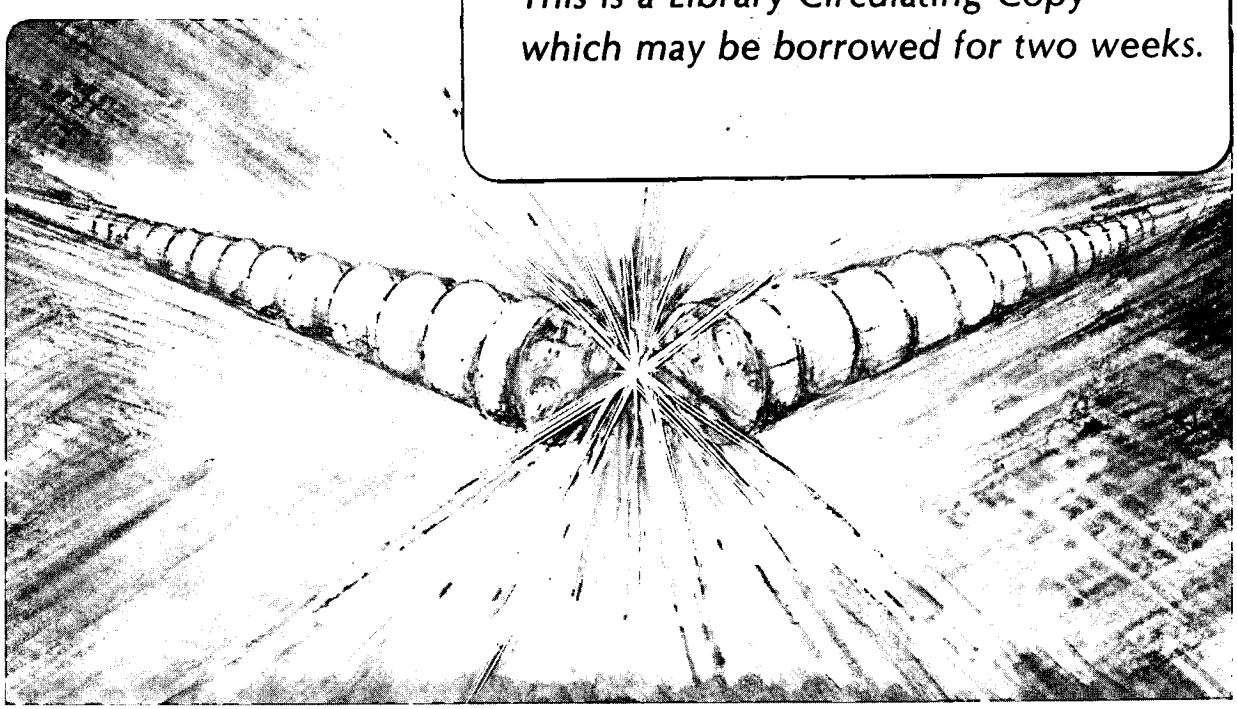

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ION BEAM MODIFICATION OF THE Y-Ba-Cu-O SYSTEM WITH THE MEVVA HIGH CURRENT METAL ION SOURCE

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ABSTRACT

We have used high-dose metal ion implantation to 'fine tune' the composition of Y-Ba-Cu-O thin films. The films were prepared by either of two rf sputtering systems. One system uses three modified Varian S-guns capable of sputtering various metal powder targets; the other uses reactive rf magnetron sputtering from a single mixed-oxide stoichiometric solid target. Film thickness was typically in the range 2000 - 5000 A. Substrates of magnesium oxide, zirconia-buffered silicon, and strontium titanate have been used. Ion implantation was carried out using a metal vapor vacuum arc (MEVVA) high current metal ion source. Beam energy was 100 - 200 keV, average beam current about 1 mA, and dose up to about 10^{17} ions/cm^2. Samples were annealed at 800 - 900°C in wet oxygen. Film composition was determined using Rutherford Backscattering Spectrometry (RBS), and the resistivity versus temperature curves were obtained using a four-point probe method. We find that the zero-resistance temperature can be greatly increased after implantation and reannealing, and that the ion beam modification technique described here provides a powerful means for optimizing the thin film

INTRODUCTION

In this paper we describe the use of ion implantation to tailor the composition of sputtered thin films of Y-Ba-Cu-O. Attaining the stoichiometric 1:2:3 ratio of Y:Ba:Cu is an important step in forming films with good superconducting properties. Sputter deposition, however, does not always transfer material congruently from target to film.

High temperature superconducting Y-Ba-Cu-O films have been produced by several variations of the sputtering process. Cosputtering - simultaneous sputtering from three sources [1-4] - offers the advantage of independent control over the flux of each metal element. Sputtering from a single target, however, is better suited to large-area uniform coating. Both stoichiometric targets [5-12] and targets compensated for film elemental deficiencies [13-18] have been used.

A number of techniques have been used to achieve more congruent transfer of elements from a stoichiometric or slightly compensated target, including the following: (1) sputtering at high pressures [5, 7-9]; (2) sputtering in pure argon [6,10,12]; (3) sputtering at low substrate temperature [8, 10-13]; (4) off-axis placement of the substrate [6-8]; (5) close source-to-substrate distance [10]; (6) use of a spherical target [11]; (7) very long pre-sputter times [12]. Methods 1, 2 and 4 reduce preferential resputtering from the film caused by negative oxygen ions, electrons, and sputtered neutrals; methods 1 and 3 reduce preferential reemission; methods 1, 5 and 6 produce a more uniform spatial distribution among the sputtered elements; and method 7 establishes steady-state conditions at the target surface. These methods, however, do not give optimum deposition rates, material usage, or film properties. Another option is to compensate the film by ion implantation during or after deposition.

In the work described here, we prepared Y-Ba-Cu-O thin films by either of two rf sputtering systems. One system was a modified Varian S-gun system using three separate 5-inch targets, capable of sputtering various metals or powders. The other system was a Leybold Heraeus Z400 using reactive rf magnetron sputtering from a single mixed-oxide stoichiometric solid target. Substrates of magnesium oxide, zirconia-buffered silicon, and strontium titanate were used in this study. Film thickness was in the range 2000 - 5000 A. Ion implantation was carried out using a metal vapor vacuum arc (MEVVA) high current metal ion source with a beam energy typically 100 - 200 keV and a mean beam current of approximately 1 mA.

ION IMPLANTATION

The MEVVA ion source is a new source whose uniqueness lies in the high current beams of metal ions that can be produced. Several different embodiments of the source have been made [19-23], including a multi-cathode version in which one can rapidly switch between any of 16 different metallic species, a miniaturized version which could be of value in research situations, and a broad-beam, very high current version. A schematic of the MEVVA II source used for the present work is shown in Figure 1.

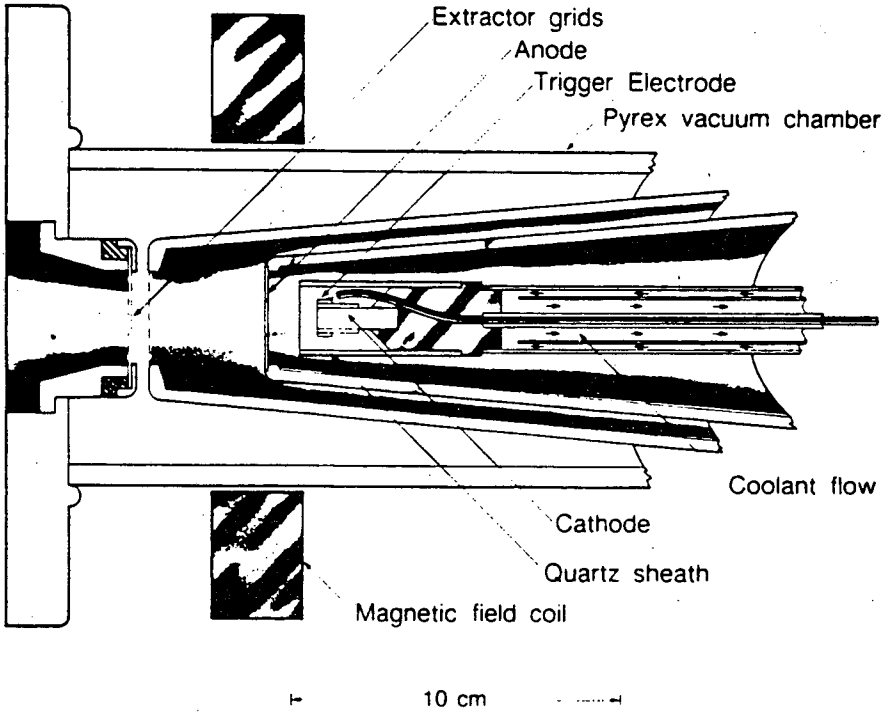

Fig. 1 Schematic of the MEVVA II ion source.

In this source, we use the intense plume of highly ionized metal plasma that is created at the cathode spots of a metal vapor vacuum arc discharge to provide the "plasma feedstock" from which the ion beam is extracted. A dense metal plasma plumes away from the cathode toward the anode and persists for the duration of the arc current drive. The anode of the discharge is located on-axis with respect to the cylindrical cathode and has a central hole through which a part of the plasma plume streams. The plasma drifts through the post-anode region to a set of grids that comprise the extractor - a three grid, accel-decel, multiaperture design.

At present the source is operated in a pulsed mode, with pulse length typically 0.25 msec and a repetition rate of up to 100 pulses per second. The source neither requires nor produces an ambient gas for its operation, and is usually run in a vacuum of around 1 x 10^{-6} Torr. The source runs cold - there is no oven, and the cathode remains solid. Beams of a wide range of ion species have been produced, including most metallic elements of the Periodic Table [22].

Implantation is done in a broad beam mode with no mass analysis. The implantation target (the Y-Ba-Cu-O sample) was positioned to face the source directly. At the target location, the ion beam is several cm wide. The MEVVA ion beam is relatively pure - ie, it contains ion species of only the cathode material - to better then 99%. The beam ions are in general multiply charged, and the charge state distribution has been studied in detail [22]. The measured charge state spectrum for a Cu ion beam is shown in Figure 2. The presence of more than a single charge state is an advantage in the present study, as it contributes to beam energy spread and consequent flatter implantation depth profile.

RESULTS

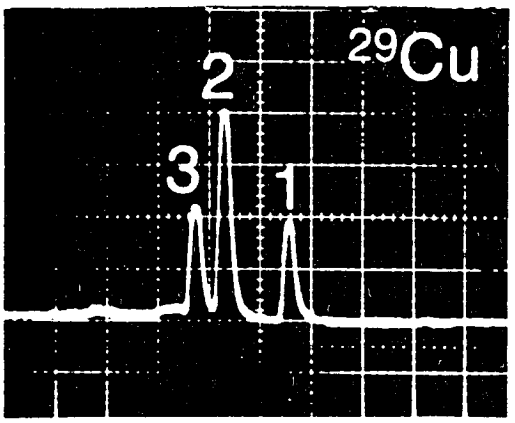

Fig. 2 Charge state spectrum of copper ion beam.

We were able to produce improved superconducting films using the stoichiometric single solid target configuration. Films were prepared on (100) $SrTiO_3$ substrates to a thickness of about 5000 A in pure argon and with a substrate temperature between 60 and 600°C. After deposition the films were annealed in flowing oxygen at 850°C for 1 hour.

The as-deposited film composition was determined by RBS and was found to be deficient in both Ba and Cu for an argon pressue of 1 4 Pa. The Ba to Y ratio was about 1.8 and insensitive to substrate temperature. The Cu to Y ratio, however, decreased rapidly as the temperature was raised from 60 to 600°C. To demonstrate the implantation technique, we investigated two films: film A was deposited at 125°C and had composition Ba:Y = 1.8 and Cu:Y = 2.0; film B was deposited at 360°C and had composition Ba:Y = 1.8 and Cu:Y = 2.5. The films were implanted with Cu with a mean beam energy of 100 keV to a dose of approximately 1×10^{17} ions/cm^2. The new Cu concentrations are estimated to be Cu:Y = 2.2 for film A and Cu:Y = 2.8 for film B. After implantation the films were reannealed.

The film resistance vs. temperature characteristic was measured using the four-point probe method. Figures 3 and 4 show the resistivity curves for films A and B (respectively) before and after implantation. For both films the resistance increases with decreasing temperature until 75°K, indicating the presence of a semiconducting phase in the normal state. After implantation and reannealing, both films exhibit a metallic behavior in the normal state. For film A, there is a feature at about 75°K that suggests the presence of a superconducting phase but without sufficient connectivity for the film to exhibit complete superconductivity; after implantation and reannealing, the film remains predominantly semiconducting at high temperatures but at much lower resistance, and there is a broad transition to superconductivity with an onset at 96°K and zero resistance at about 40°K. Film B shows better pre-implantation resistance-temperature properties because the initial Cu content was higher; after implantation and reannealing there is a change to more metallic behavior, and a superconducting transition onset at 95°K with zero resistance at 60°K.

Unfortunately, remnants of the silver paint used to attach the four point probe interfered with the post-implantation set of RBS measurements, and so the before and after RBS data are not available for this preliminary experiment. RBS data will be obtained in future work.

To eliminate the possibility that the effects we have observed could have been caused simply by the second annealing step, we annealed similarly formed films twice, but without the intermediate ion implantation. In these cases the zero resistance temperature of the films decreased by a few degrees only. Thus the improved film properties are due to the change in composition brought about by ion implantation.

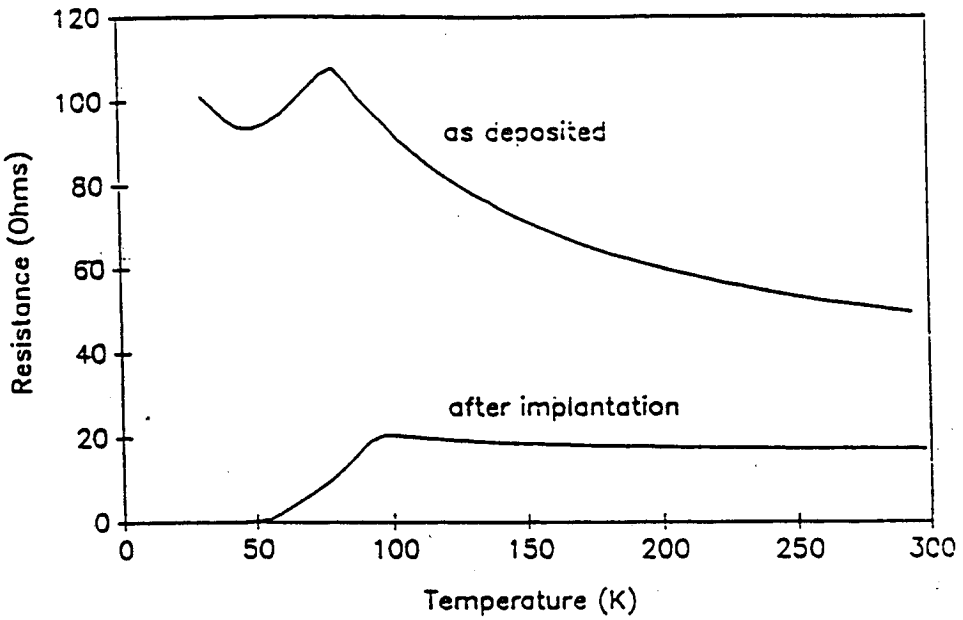

Fig. 3 Resistance vs. temperature of Y-Ba-Cu-O film before and after ion implantation of Cu. Y:Ba:Cu = 1:1.8:2.0 as deposited; the Cu fraction was increased to Cu:Y = 2.2 after implantation.

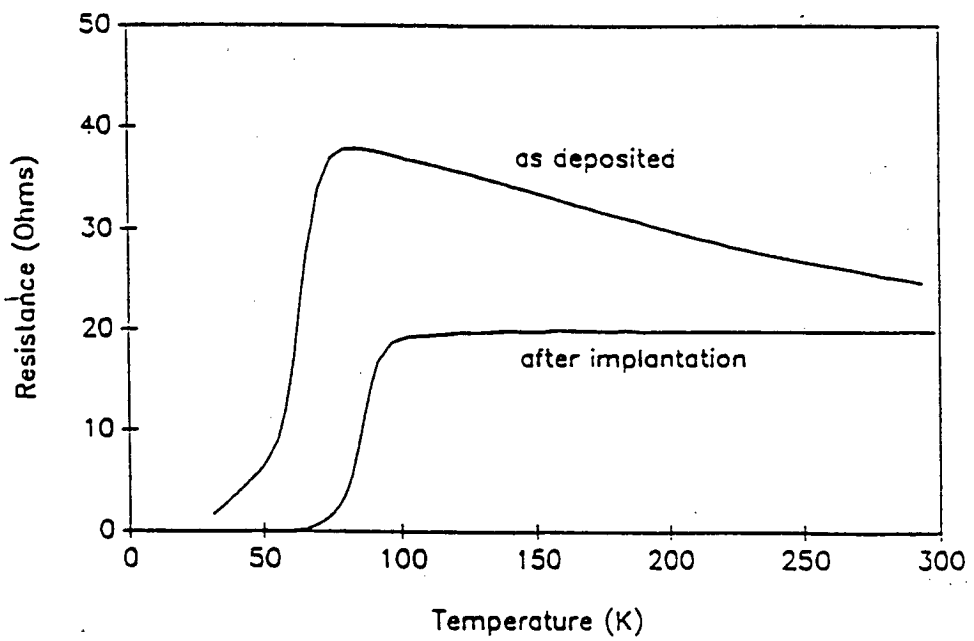

Fig. 4 Resistance vs. temperature of Y-Ba-Cu-O film before and after ion implantation of Cu. Y:Ba:Cu = 1:1.8:2.5 as deposited; the Cu fraction was increased to Cu:Y = 2.8 after implantation.

ACKNOWLEDGMENT

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