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Ion Implantation of Sputtered Y-Ba-Cu-O Films

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Abstract

Thin films of Y-Ba-Cu-O were deposited by rf magnetron sputtering from a single stoichiometric target and then altered in composition by ion implantation. Under optimum deposition conditions the films are deficient in Ba and Cu. Ion implantation of Cu was performed using a metal-vapor vacuum-arc source having high current and a broad energy spectrum for good depth distribution. Composition was determined by Rutherford backscattering spectrometry. The zero-resistance temperature was greatly increased after implantation and reannealing. This method could be used to write superconducting patterns on insulating material.

This paper describes the use of ion implantation to produce superconductivity in sputtered Y-Ba-Cu-O films. Attaining the stoichiometric 1:2:3 ratio of Y:Ba:Cu is an important first step in depositing films with good superconducting properties. Sputter deposition, however, does not always transfer material congruently from target to film. Ion implantation could be used to compensate for elements deficient in the film. This technique could then be used to write superconducting patterns on insulating films for device fabrication.

Ion implantation damage has been found to destroy superconductivity in Y-Ba-Cu-O thin films^{1,2}. Koch et al.³ made use of this effect to create regions of normal material in a superconducting film, thereby fabricating a superconducting quantum interference device. Nastasi et al.⁴ took the opposite approach, implanting Y in BaF₂-Cu films and rendering them superconducting with a subsequent anneal.

High-temperature superconducting Y-Ba-Cu-O films have been produced by several variations on the sputtering process. Cosputtering, that is simultaneous sputtering from three sources,⁵⁻⁷ offers the advantage of independent control over the flux of each metal element. Sputtering from a single target⁸⁻¹⁰, however, is better suited to large-area uniform coating. Our films were made by r.f. sputtering from a stoichiometric oxide target onto (100) SrTiO₃ substrates. The thickness of each film was about 5000 Å deposited at 1 Å/s. The films were deposited at pressures of 1.3-8.0 Pa of pure argon at various substrate temperatures between 60 to 600 C. After deposition, the films were annealed in flowing oxygen at 850 C for 1 hour.

Composition was determined by Rutherford Backscattering Spectrometry (RBS). When using 2-MeV He ions the elemental peaks overlapped, obscuring information from all but the top 1000 Å of the films. The surface portion of the films, at least, appeared to be quite uniform, and compositions were estimated simply from the

height of the peak edge. At a pressure of 1.3 Pa the films were found to be deficient in both Ba and Cu. The ratio of Ba to Y 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. Film A, deposited at 125 C, had Ba/Y=1.8 and Cu/Y=2.0. Film B, deposited at 360 C, had Ba/Y=1.8 and Cu/Y=2.5.

Ion implantation was accomplished using a metal-vapor vacuum arc (MEVVA) high-current ion source.¹¹ A schematic of the MEVVA II source used in this work is shown in Figure 1. An intense plume of highly ionized metal plasma is created at the cathode spots of the vacuum arc discharge. Part of the plasma streams through a central hole in the anode which is located on axis with respect to the cylindrical cathode. The plasma plume drifts towards the extractor which consists of three grids.

This source can produce intense pulsed ion beams of a wide range of metal species.¹² The two films described above were implanted with Cu to bring the Cu/Y ratio closer to the stoichiometric value of 3. Beams of Y have also been produced and could be used for compensating Y-deficient films, but we cannot presently compensate for Ba by this method. The Cu implantation was performed in a broad-beam mode (a direct beam from source to target, without magnetic analysis) at a mean beam energy of 100 keV and an ion current density at the film of 15 mA/cm². The source was repetitively pulsed in order to accumulate a total Cu-ion dose of approximately 10¹⁷ ions/cm².

In the broad-beam mode the beam was several cm wide at the target location. The ion beam contains a mixture of charge states and so has a broad energy spectrum producing a relatively flat implantation depth profile. The measured charge spectrum for a Cu beam shows the +1, +2, and +3 charge states are present in the approximate ratio 1:2:1. For an extraction voltage of 50 kV, the beam is composed of groups

of ions having energies of 50 keV, 100 keV and 150 keV. The range and straggling for the Gaussian implanted concentration are calculated¹³ and listed in Table 1.

Resistance versus temperature was measured using a four-point probe after each anneal. After careful removal of the silver paint from the first set of measurements the new Cu concentrations were measured to be $\text{Cu}/\text{Y}=3.0$ for film A and $\text{Cu}/\text{Y}=3.3$ for film B at the surface. Calculated values, however, are $\text{Cu}/\text{Y}=2.2$ for film A and $\text{Cu}/\text{Y}=2.8$ for film B, assuming that the implanted dose was distributed uniformly throughout the film after annealing. The nonuniformity indicated by the difference in measured and calculated values is not apparent in the 1000-A region directly observable with RBS.

Figure 2 shows the resistance of film A before and after ion implantation. There is a feature in the curve at about 75 K that suggests the presence of a superconducting phase but without sufficient connectivity for the film to have complete superconductivity. After reannealing, the film remains predominantly semiconducting at high temperatures, but with a much lower resistance. Also, there is a broad transition with an onset at 96 K zero resistance at about 40 K.

Film B had a higher initial Cu content and Figure 3 shows superior properties to film A as deposited. This film was semiconducting at high temperatures and had a transition from 72 with a broad tail to about 20 K. This film also shows a change to more metallic behavior after implantation with a superconducting transition from 95 to 60 K.

It is possible that the effect described above could have been caused in part by the second annealing step. To eliminate this possibility, similarly deposited films were annealed twice without the intermediate ion implantation. In these cases, the zero-resistance temperature of the films decreased by a few degrees, indicating that the

improvements in film properties were due to the change in composition caused by implantation.

Ion bombardment has been found to destroy superconductivity at doses as low as 10^{14} ions/cm².¹ This is believed to be caused by formation of an amorphous layer at grain boundaries. Thermal annealing after ion irradiation causes irreversible compositional changes near the film surface.^{14,15} We do not observe such severe segregation in our films even though our doses and annealing temperatures are relatively high. White et al.¹⁶ find that the damage to the films is greater when they are implanted below 90 K. Our films may have escaped this level of damage because they were implanted at room temperature.

The above results show that a Y-Ba-Cu-O film can be compensated for a Cu deficiency by ion implantation with a significant improvement in zero-resistance temperature. Better results may result with closer approach to the stoichiometric composition.

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Figure Captions

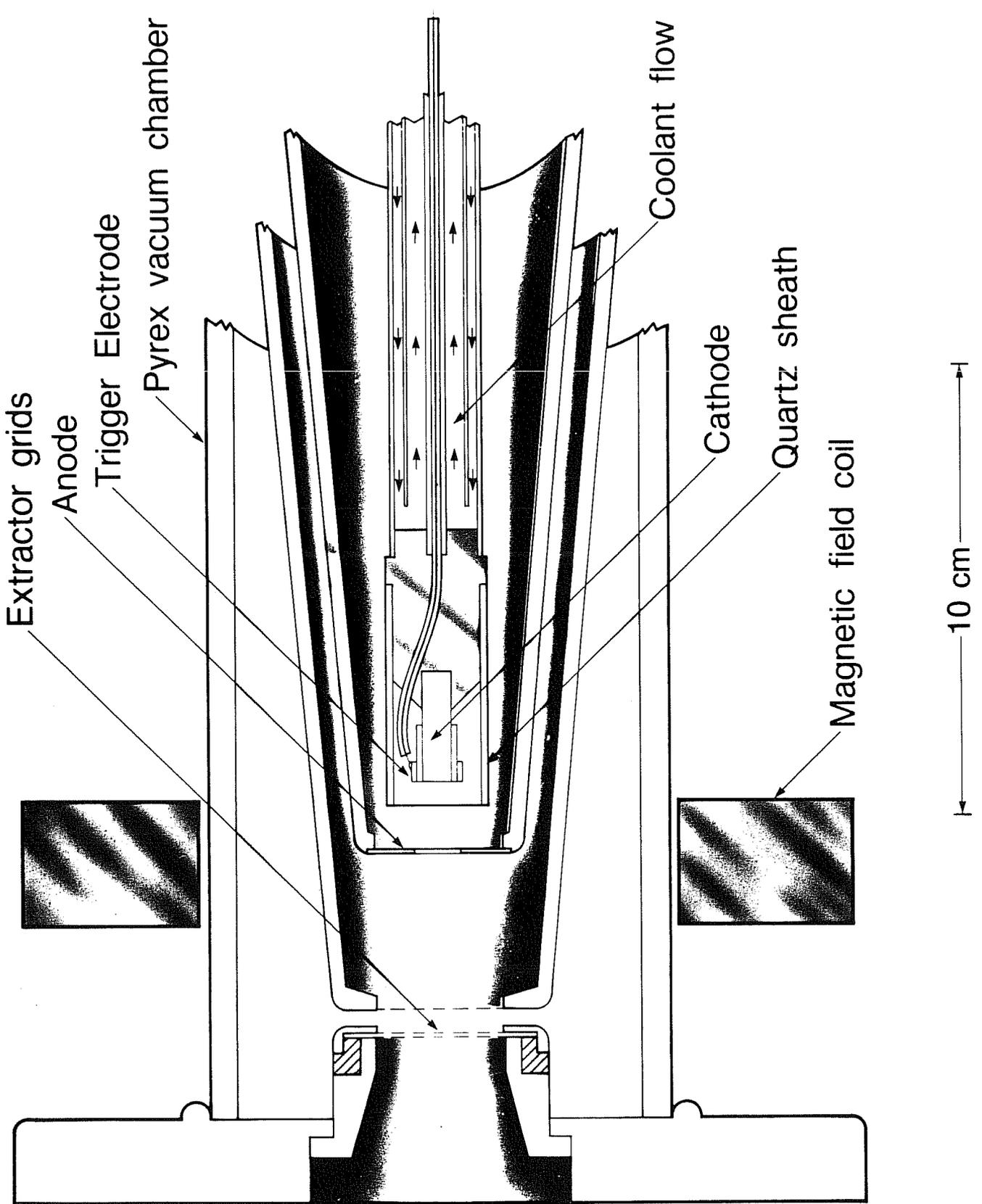
Figure 1. Schematic of the MEVVA II ion source.

Figure 2. Resistance versus temperature of a Y-Ba-Cu-O film before and after ion implantation of Cu. The composition ratios were Ba/Y=1.8 and Cu/Y=2.0 as deposited increasing to Cu/Y=2.2 after implantation.

Figure 3. Resistance versus temperature of a Y-Ba-Cu-O film before and after ion implantation of Cu. The composition ratios were Ba/Y=1.8 and Cu/Y=2.5 as deposited increasing to Cu/Y=2.8 after implantation.

Table 1. Calculated implantation profiles for Cu ions in various charge states.

Voltage	Charge	Energy	Range	Stragglng
kV		keV	A	A
50	+1	50	360	170
50	+2	100	650	285
50	+3	150	960	400



Extractor grids

Anode

Trigger Electrode

Pyrex vacuum chamber

Coolant flow

Cathode

Quartz sheath

Magnetic field coil

10 cm

