LA-UR--90-4069

DE91 004867

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DEC 13 1990

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SUBMITTED TO: Materials Research Society Fall Meeting
Boston, MA
November 26-30, 1990

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SUPERCONDUCTING YBaCuO THIN FILMS BY Cu-ION IMPLANTATION

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ABSTRACT

We have investigated the fabrication of thin-film superconductors by Cu-ion implantation into initially Cu-deficient $\text{Y}(\text{BaF}_2)\text{Cu}$ thin films. The precursor films were co-evaporated on SrTiO_3 substrates, and subsequently implanted to various doses with 400 keV $^{63}\text{Cu}^{2+}$. Implantations were performed at both LN_2 temperature, and at 380°C . The films were post-annealed in oxygen, and characterized as a function of dose by four-point probe analysis, X-ray diffraction, ion-beam backscattering and channeling, and scanning electron microscopy. It was found that a significant improvement in film quality could be achieved by heating the films to 380°C during the implantation. The best films became fully superconducting at 60-70 K, and exhibited good metallic R vs. T. behavior in the normal state.

INTRODUCTION

High quality $\text{YBa}_2\text{Cu}_3\text{O}_{7-8}$ thin films are now routinely grown at a number of laboratories worldwide, and research is now focusing on the development of practical applications such as IR detectors, rf cavities, and micro-electronic devices. In the field of device fabrication, the prospects for integration of the high-temperature oxide superconductors as circuit interconnects, SQUIDS, hybrid semiconductor/superconductor circuits, etc., appear promising. The possibility of device fabrication employing standard ion-beam technology has already been demonstrated by several research groups [1-3].

In one experiment, Nastasi et al.[3] implanted Y ions into a thin film of composition $(\text{BaF}_2)_2\text{Cu}_3$. Upon annealing, the precursor material became an insulator, but the Y-implanted material became a superconductor with an onset temperature of 85 K, and $T_{c,r=0} \approx 35$ K. This result raises the possibility that patterned superconductors could be fabricated by direct writing, using existing focused ion-beam technology.

We have performed a complementary series of experiments, using Cu-ion implantation into Cu-deficient $\text{Y}(\text{BaF}_2)\text{Cu}$ thin films. The motivation for implanting Cu, despite the increased dose required, was the reduction in nuclear stopping power and sputtering yield associated with the lighter projectile. The decreased sputtering yield implies that, depending on the initial Cu concentration, less of the as-deposited film will be sputter etched during the implantation. The decrease in nuclear stopping power leads to an increase in the incident-ion range, allowing greater flexibility in choosing the film thickness. Furthermore, any ions reaching the film/substrate interface will cause less damage to that critical region. The electrical and structural properties of the as-deposited and implanted films were investigated as a function of implant dose using a variety of analytical techniques.

EXPERIMENTAL PROCEDURE

Thin films of $\text{Y}(\text{BaF}_2)\text{Cu}$ were deposited by electron-beam co-evaporation onto substrates of $\langle 100 \rangle$ SrTiO_3 . The substrates remained at ambient temperature during the evaporation. Films were simultaneously deposited onto $\langle 100 \rangle$ MgO , for ion-backscattering measurements of thickness and metals composition. Typical film thicknesses, before implantation, were 5000-5500 Å. Several initial compositions were investigated, with Cu/Y ratios ranging from 0.6-1.6. The Cu concentrations were chosen to correspond to regions of the ternary phase diagram where only non-superconducting phases have been observed [4]. The Ba concentration was also varied to account for the observed preferential sputtering of this species.

The as-deposited films were implanted with 400 keV $^{63}\text{Cu}^{2+}$ ions. The implant doses ranged from $0.82\text{-}4.0 \times 10^{17}$ ions/cm², with typical beam currents of $4\text{-}5 \mu\text{A/cm}^2$. The projected ion range for the as-deposited films was calculated to be 1850 ± 715 Å, well below the initial film thicknesses [5]. Implantations were performed for samples held at both LN_2 temperature, and at 380°C . White et al.[6] have demonstrated that temperatures as low as 400°C are sufficient to re-crystallize SrTiO_3 amorphized by Pb-ion irradiation. It was therefore anticipated that the higher implantation temperature would reduce potential structural damage at the film/substrate interface.

After implantation, the films deposited on SrTiO₃ were furnace annealed. The anneal protocol for all samples was: 750°C for 1 hr in flowing dry oxygen; 850°C for 1 hr in flowing wet oxygen; slow cooling in flowing dry oxygen.

The resistance vs. temperature characteristics of the annealed films were measured by a standard dc four-point probe apparatus. In addition, ion channeling measurements were performed to determine the degree of epitaxial film growth during the post-implantation anneal. The crystal structure of the films was determined by X-ray diffraction (XRD) measurements, and film morphology was observed by scanning electron microscopy (SEM).

RESULTS

The compositions of the as-deposited films were chosen to obtain the maximum possible Cu concentrations while still producing, upon annealing, only non-superconducting phases. The bulk ternary phase diagram for the Y-Ba-Cu-oxide system was found to be unsuitable as a guide for this purpose. Contrary to expectation, as-deposited films of composition YBa_{2.0}Cu_{1.5} and YBa_{1.9}Cu_{0.89} were found to contain a significant fraction of superconducting material after annealing. The Cu concentration was therefore further decreased. Results are presented below for two of these depositions, illustrating the effects of increasing the sample temperature during the implantation.

Deposition A - LN₂ temperature implantation:

The initial film composition was intentionally Ba rich, YBa_{3.0}Cu_{0.53}, to account for the preferential sputtering of this species observed during preliminary low-temperature implantations. Upon annealing, the as-deposited film was found to be an insulator, as desired. SEM observations show the film to consist of randomly oriented needle-shaped grains, with plate-shaped grains interspersed. An XRD analysis indicated the presence only of BaCuO₂ and YBa-oxides.

The films were implanted to doses of 1.1, 2.2, 3.0, and 4.0 x 10¹⁷ ion/cm², at LN₂ temperature. The resulting film compositions, measured by ion backscattering, are summarized in Table 1; the preferential sputtering of Ba is evident. Four-point probe data for the implanted films are shown in Figure 1. The film implanted to the *lowest* dose exhibited the highest transition temperature, with T_{c, on} = 90 K, and T_{c, R=0} = 70 K. However, the relatively high normal-state resistance suggests that the volume fraction of superconducting material in this sample is small. The higher dose films have reduced transition temperatures of T_{c, R=0} ≈ 50 K, and, furthermore, sample A5 (closest to the nominal 123 composition) exhibits a semiconductor R vs. T behavior above T_c. The low transition onset temperatures for these films suggest that the superconducting phase is oxygen deficient, possibly the so-called ortho-II phase with T_c ≈ 60 K [7].

In contrast to the four-point probe data, structural analyses indicate that the crystalline quality of the films improves with increasing implant dose. SEM photographs show that the film morphology evolves into the basket-weave structure indicative of a/b-axis oriented 123 material. This is also evident from the XRD data, and c-axis oriented material was detected in the films with the two highest implant doses. Clearly the volume fraction of superconducting material increases with implantation dose, although the quality of the material evidently decreases.

Ion-channeling data obtained for these films are presented in Figure 2. Sample A5, with composition YBa_{2.5}Cu_{3.2}, exhibited the best channeling yield of χ_{min} ≈ 0.91. The data indicate that little epitaxial growth occurred during the post-implantation anneal.

Deposition B - 380°C implantation:

The preferential sputtering of Ba observed during the low-temperature implantations was not as pronounced at 380°C. Therefore the Ba concentration for this set of films was reduced, with an as-deposited composition of YBa_{2.1}Cu_{0.59}.

Films were implanted to doses of 1.0, 2.0, and 3.8 x 10¹⁷ ion/cm². The resulting film compositions are summarized in Table 1. Four-point probe data for these films are shown in Figure 3. Upon annealing, the as-deposited film was found to exhibit a resistive transition with an onset at 80 K, and an offset at 74 K. However, the sample did not become fully superconducting down to 29 K. Evidently, the superconducting volume fraction was sufficiently small that a continuous conducting pathway was not present. Sample B4, closest to the nominal 123 composition, exhibited the best R vs. T characteristics, with a transition onset

at 80 K, and $T_{c,R=0} = 61$ K. In contrast, sample B3 exhibited resistive transitions at ≈ 80 K and at ≈ 68 K, but was not fully superconducting down to 29 K, and sample B2 was found to be an insulator.

A weak XRD pattern confirmed the presence of the 123 and 248 phases in the as-deposited (plus annealed) film. Similar diffraction patterns were observed for samples B2 and B3. However, the pattern for sample B4 was found to be quite strong, and indicated a high degree of c and a/b axis orientation. SEM photographs show an evolution in morphology similar to that observed for Deposition A, with sample B4 exhibiting the familiar basket-weave structure, intermixed with regions of c-axis oriented growth.

Channeling measurements for these films are illustrated in Figure 4. No channeling was detected near the surface of the as-deposited film. However, a reduced yield of $\chi \approx 0.7$ was observed near the film/substrate interface. This suggests that crystal growth during the anneal proceeded outward from the interface, terminating when un-reacted material of the correct stoichiometry was no longer available. Channeling was not detected for sample B3. However, sample B4 exhibited a reduced yield of $\chi = 0.56$ integrated over the depth of the film. In this case, the degree of disorder was found to increase near the film/substrate interface. This may result from penetration of Cu ions into the SrTiO_3 substrate during the implantation.

DISCUSSION

The results confirm that thin-film superconductors can be fabricated by ion-implantation alloying, and that it may be possible to synthesize patterned superconducting devices by direct ion implantation. However, the bulk ternary phase diagram was not useful for predicting the properties of the films deposited in this experiment. As exemplified by sample B1, with a composition of $\text{YBa}_{2.1}\text{Cu}_{0.59}$, inclusions of superconducting material may be formed even in very highly Cu deficient films. This may imply an advantage for Y implantation, where it is convenient to employ binary alloys as precursors.

As seen from Table 1, the preferential sputtering of Ba was nearly eliminated by increasing the sample temperature during implantation. It may be noted that based on energy sharing within the collision cascades, Y is predicted to sputter preferentially with respect to Ba [8]. Evidently chemical or thermodynamic effects dominate in this case. In addition to a lower cohesive energy, Ba metal has a much lower surface free-energy than either Cu or Y [9,10]. The observed preferential sputtering may therefore be the result of thermodynamic segregation of Ba to the film surface. Li and Koshikawa [11] have studied AuCu alloys and determined that, under ion bombardment conditions comparable to those in the present experiment, atomic mobility was sufficiently enhanced for thermodynamic surface segregation to occur at temperatures as low as 150 K. Because the degree of equilibrium segregation is predicted to decrease as the sample temperature is increased [12], the increase in implantation temperature to 380°C would be expected to reduce the degree of preferential sputtering, consistent with observation.

There are additional benefits from increasing the sample implantation temperature. Sputtering during the highest dose implantations typically reduced the film thicknesses to ≈ 3000 Å, so that some Cu ions may have reached the film/substrate interface. The resulting damage to the substrate lattice could prevent epitaxial crystallization of the film during the subsequent oxygen anneal [13]. White et al. [6] have investigated the response of ion-beam damaged SrTiO_3 to low-temperature anneals. It was found that a temperature of 400°C was sufficient to re-crystallize the amorphous layers at a growth rate of ≈ 8 Å/s. Therefore, the increased implantation temperature in the present experiment should at least partially eliminate substrate damage near the interface region before the oxygen anneal, improving the epitaxial quality of the final films. The ion-channeling data in Figs. 2 and 4 do provide evidence for this.

Finally, the increased atomic mobility at the higher implantation temperature may result in a greater pre-anneal depth uniformity for the Cu concentration. This would improve the phase uniformity and structural characteristics of the final films, and thus their transport properties.

Ion-backscattering analysis indicated that a number of the samples underwent significant film/substrate interdiffusion during the annealing procedure. Generally, the degree of interaction was found to be greatest for the un-implanted films, and to *decrease* with increasing implant dose (and Cu concentration). It is therefore not the result of ion-beam induced damage at the film/substrate interface. Although material with the 123 stoichiometry reacts very little with SrTiO_3 [14], this is evidently not the case for material highly deficient in Cu.

The results as a whole indicate that neither superconducting phase formation, nor formation of secondary phases, can be easily controlled using the technique of ion implantation alloying. The initial film composition, implanted ion distribution, preferential sputtering of the film during implantation, and radiation damage at the substrate surface, all contribute in a complex manner to the final state of the annealed films.

CONCLUSIONS

The data show that thin-film high-temperature superconductors can be fabricated by Cu-ion implantation into initially Cu-deficient films. Upon annealing in an oxygen atmosphere the implanted films are superconducting, while, depending on the initial Cu concentration, the precursor material is insulating. The quality of the films is improved significantly by performing the implantations at an elevated temperature. This nearly eliminates preferential sputtering of Ba, and ion-beam induced damage near the substrate surface is at least partially annealed, facilitating epitaxial growth during the post-implantation anneal.

The authors would like to acknowledge discussions with Alice White (AT&T Bell Labs), and the technical assistance of Mark Hollander and Caleb Evans. The ion-beam analysis was performed at the LANL Ion Beam Materials Laboratory, and the work was supported in part by the LANL/DOE Superconductivity Pilot Center.

REFERENCES

- [1] R.H. Koch, C.P. Umbach, G.J. Clark, P. Chaudhari, and R.B. Laibowitz, *Appl. Phys. Lett.* **51**, 200 (1987).
- [2] K.T. Short et al., *Bull. Am. Phys. Soc.* **33**, 779 (1988).
- [3] M. Nastasi, J.R. Tesmer, M.G. Hollander, J.F. Smith, and C.J. Maggiore, *Appl. Phys. Lett.* **52**, 1729 (1988).
- [4] K.Y. Yang, H. Homma, R. Lee, R. Bhadra, M. Grimsditch, S.D. Bader, J.P. Locquet, Y. Bruynseraede, and I.K. Schuller, *Appl. Phys. Lett.* **53**, 808 (1988).
- [5] TRIM89, see J.F. Zeigler, J.P. Biersack, and U. Littmark, *The Stopping and Range of Ions in Solids*, (Pergamon Press, New York, 1985).
- [6] C.W. White, L.A. Boatner, P.S. Sklad, C.J. McHargue, J. Rankin, G.C. Farlow, and M.J. Aziz, *Nucl. Instr. Meth.* **B32**, 11 (1988).
- [7] P. Bordet, C. Chaillout, J. Chenavas, J.L. Hodeau, M. Marezio, J. Karpinski, and E. Kaldis, *Nature* **334**, 596 (1988).
- [8] P. Sigmund, in *Sputtering by Particle Bombardment I*, ed. R. Behrisch (Springer-Verlag, New York, 1981) p.9.
- [9] C. Kittel, *Introduction to Solid State Physics*, (John Wiley and Sons, New York, 1976).
- [10] A.R. Miedema, *Z. Metallkde.* **69**, 287 (1978).
- [11] R.S. Li and T. Koshikawa, *Surf. Sci.* **151**, 459 (1985).
- [12] J.C. Hamilton, *Phys. Rev. Lett.* **42**, 989 (1979).
- [13] N. Bordes, M. Cohen, M. Nastasi, A.D. Rollett and C.J. Maggiore, *Thin Solid Films* **181**, 191 (1989).
- [14] H. Koinuma, K. Fukuda, T. Hashimoto, and K. Fueki, *Jap. J. Appl. Phys.* **27**, L1216 (1988).

Figure 1: Resistance vs. temperature data for the films from a) Deposition A, and b) Deposition B, as a function of implantation dose.

Figure 2: Ion-beam channeling data for the annealed films from a) Deposition A, and b) Deposition B, as a function of implantation dose. The incident beam was 8.8 MeV He, with a scattering angle of 166°.

Table 1: A summary of film composition as a function of Cu-ion implantation dose for the sample sets studied in this experiment.

	Sample #	Implant Dose ($\times 10^{17}$ ion/cm ²)	Y : Ba : Cu
Deposition A	1	as-dep	1 : 3.0 : 0.53
	2	1.1	1 : 2.8 : 1.2
	3	2.2	1 : 2.8 : 1.8
	4	3.0	1 : 2.7 : 2.4
	5	4.0	1 : 2.5 : 3.2
Deposition B	1	as-dep	1 : 2.1 : 0.59
	2	1.0	1 : 2.0 : 0.95
	3	2.0	1 : 2.0 : 1.5
	4	3.8	1 : 2.0 : 2.6

Table 1

Fig 1a

Fig. 1b

Figure 2a

Figure 2h

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