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Citation: Applied Physics Letters **52**, 2077 (1988); doi: 10.1063/1.99752 View online: http://dx.doi.org/10.1063/1.99752 View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/52/24?ver=pdfcov Published by the AIP Publishing

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Superconducting oxide films with high transition temperature prepared from metal trifluoroacetate precursors

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(Received 6 April 1988; accepted for publication 21 April 1988)

Superconducting thin films of Y-Ba-Cu oxide have been prepared on yttria-stabilized zirconia substrates using metal trifluoroacetate spin-on precursors. The films exhibit an extremely sharp resistive transition with zero resistance at temperatures as high as 94 K. The superconducting phase is formed by a three-step process: (a) decomposition of the spun-on trifluoroacetate film to the fluorides, (b) conversion of the fluorides to oxides by reacting with water vapor, and (c) annealing followed by slow cooling in oxygen. The properties of the films depend on the amount of conversion of the fluorides by reaction with water. Films which show the presence of some unreacted barium fluoride have strong c-axis normal preferred orientation, with a sharp resistive transition. When all the barium fluoride is converted, the film is more randomly oriented and exhibits a broader transition to zero resistance.

Since the discovery of superconductivity at high temperatures in copper oxide perovskites, deposition of thin films of the materials has been demonstrated using a variety of vacuum and nonvacuum techniques.¹⁻⁴ While bulk samples of the $Y_1Ba_2Cu_3O_7 = \delta$ (1-2-3) superconductor which exhibit complete superconductivity at temperatures around 90 K with 1-2 K transition width can be prepared routinely, it is much more difficult to prepare thin films with such high transition temperatures. This is primarily due to interaction of the film with the substrate during annealing, which leads to substitution and formation of unwanted phases in the film. Difficulty in controlling the exact composition during deposition, and sensitivity of barium oxide to H_2O and CO_2 , also cause formation of secondary phases. All of these factors result in broadening the resistive transition, even though the onset temperature may remain unaffected.

Solution precursors of Y, Ba, and Cu, like nitrates^{2,3} and different carboxylates,⁴ have been used for preparation of superconducting films of 1-2-3 by nonvacuum techniques. The solution is sprayed or spun-on to the substrate and converted to the oxides by thermal decomposition at temperatures of 300–500 °C. The crystalline superconducting phase is formed by subsequent annealing in oxygen at a higher temperature. Besides process simplicity, the use of solution precursors allows accurate control of composition and intimate mixing of the constituents. However, carbon contamination during decomposition (of carboxylates) and reactivity of the intermediate barium oxide result in formation of superconducting films with fairly broad transition.

We have used a spin-on solution containing a mixture of Y, Ba, and Cu trifluoroacetates (TFA) to prepare superconducting films of yttria-stabilized zirconia (YSZ) substrates which exhibit an extremely sharp resistive-to-superconducting transition and have zero resistance at temperatures higher than 90 K. Unlike nitrate and carboxylate precursors, the trifluoroacetates decompose primarily to the fluorides which are much less sensitive to moisture and carbon contamination. The advantage of using BaF_2 in place of a Ba metal source for preparing superconducting films with reproducible properties by coevaporation has been noted before.⁵ By using precursors of Y, Ba, and Cu, which provide fluoride

intermediates, we have achieved zero resistance in thin films at a temperature as high as 94 K, which is one of the highest values reported for films of Y-Ba-Cu oxide.

The yttrium and barium trifluoroacetates [Y(TFA), and $Ba(TFA)_2$ were prepared by reacting Y_2O_3 and BaCO₃, respectively, with aqueous trifluoroacetic acid (CF₃COOH) and evaporating to dryness. Cu(TFA)₂ was prepared by reacting Cu metal with trifluoroacetic acid in the presence of hydrogen peroxide. Thermogravimetric analysis of the individual trifluoroacetates (4 °C/min) carried out in argon atmosphere shows that they slowly lose their water of crystallization between 50 and 200 °C, and then all of them decompose fairly readily around 300 °C. The decomposition temperatures are lowered by as much as 30-70 °C when the decomposition is carried out in oxygen atmosphere. The weight loss and x-ray analysis of the powders decomposed in argon show that Y(TFA), and Ba(TFA), decompose to the respective fluorides, YF₃ and BaF₂. Cu(TFA)₂ forms a mixture of CuF₂, Cu₂O, and CuO. A small amount of an air-sensitive volatile solid, which we have not identified, is also formed during decomposition of Cu(TFA)₂. Fluoride decomposition products are also observed for Y(TFA)₃ and Ba(TFA)₂ when the decomposition is carried out in oxygen atmosphere, whereas Cu(TFA)₂ decomposes to form CuF₂ and CuO. Formation of fluorides by decomposition of rare-earth trifluoroacetates has been reported in an earlier study.6 The volatile products which were identified include (CF3CO)2O, CO2, CO, and some secondary decomposition products. For the 1-2-3 mixture of Y-Ba-Cu trifluoroacetates, we observe complete decomposition at a temperature of 340 °C in argon atmosphere, with a weight loss of 64%. No further weight change is observed up to 900 °C. In an oxygen atmosphere, complete decomposition occurs at around 310 °C with similar weight loss.

The fluorine substitution makes all the three trifluoroacetates readily soluble in a variety of organic solvents, including alcohols. We prepared the solution in methyl alcohol for spin-on application on single-crystal substrates of yttria-stabilized zirconia. Both (100) oriented and randomly cut substrates were used for the study. The concentration

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was adjusted so as to produce ~ 3 - μ m-thick films at a spin speed of 2000 rpm. The spun-on films are amorphous, as determined by x-ray, and are featureless. The films are decomposed by slowly heating them in air to a temperature of 400 °C. X-ray pattern shows that the films are still mostly amorphous after this step, with some broad diffraction peaks that can be assigned to BaF₂. The film thickness after decomposition is 1.0–1.1 μ m. A second layer is spun on and decomposed to build up the thickness to $\sim 2 \mu$ m.

To form the superconducting phase, a typical sample is heated in an oven at 850 °C for 30 min under flowing helium saturated with water vapor. Helium is bubbled through water at room temperature to introduce the water vapor into the oven. This is followed by a short anneal (5-10 min) in dry helium at temperatures of 900-920 °C. The helium flow is then stopped and replaced by dry oxygen flow, and the oven is shut off. The sample is then allowed to cool in the presence of flowing oxygen over a period of 3 h to below 200 °C before being removed from the oven (procedure 1). The short anneal at 900-920 °C is required for sharpening the superconducting transition as will be described later. The thickness of the superconducting film is $0.8-1.0 \ \mu m$. Some superconducting films were also prepared by directly heating the sample in presence of moist helium at 920 °C for 5-10 min and then slowly cooling in oxygen (procedure 2). We have found that water vapor is essential to converting the fluorides to oxides through formation of hydrogen fluoride. An insulating mixed fluoride phase is formed by heating in helium or oxygen alone. The films produced by directly reacting with water at 920 °C tend to be rougher as compared to films reacted at 850 °C and then annealed at the higher temperature. This probably is a result of enhanced reactivity at the higher temperature. Elemental analysis of the films by inductively coupled plasma emission spectroscopy shows the relative concentration of Y:Ba:Cu to be within 5% of 1:2:3.

X-ray diffraction patterns of films annealed using the two different procedures are shown in Figs. 1(a) and 1(b). The major peaks in the pattern correspond to the (00/) reflections of the superconducting oxide phase, indicating a strong c-axis normal preferred orientation. Barium fluoride and an unidentified third phase, with Bragg peaks (Cu $K\alpha$ radiation) occurring at $2\Theta \sim 15.66$, 31.53, and 65.77, are also present. The fraction of the unidentified phase is much lower when the film is reacted in presence of water at 920 °C [Fig. 1(a)]. It is interesting to note that in both cases the barium fluoride is also textured with enhanced (111) reflection. The [111] long diagonal in the BaF₂ unit cell is only 1.5% shorter than twice the [110] diagonal in the 1-2-3 unit cell, which may lead to mutual preferred orientation of the two phases. When the film is reacted with water for a longer period to convert all the barium fluoride, the preferential orientation of the 1-2-3 phase is significantly reduced [as seen in Fig. 3(c)]. The unidentified phase is, however, still present. Similarly, when the films are heated directly at 920 °C in the presence of water for a longer period, it results in the formation of only the 1-2-3 phase with random orientation. Thus preferential orientation of the 1-2-3 phase only occurs in the presence of barium fluoride. The high degree of



FIG. 1. X-ray diffraction patterns of superconducting films prepared using different annealing procedures: (a) procedure 2, 920 °C (10 min); (b) procedure 1, 850 °C (30 min), 920 °C (5 min); and (c) procedure 1, 850 °C (60 min), 920 °C (5 min). The prominent peaks observed for the 1-2-3 phase are labeled in (a), BaF₂ peaks are labeled in (b), and unidentified peaks marked by * in (c). Note that the vertical scale has been expanded $\times 5$ in (c).

texture is apparent from the scanning electron micrograph shown in Fig. 2(a). The grains grow as large interconnected platelets which lie parallel to the surface. Smaller grains with spheroidal morphology decorate the surface of the platelets. Energy dispersion x-ray analysis shows that these grains contain a large fraction of barium and are believed to be rich in barium fluoride. These grains are noticeably absent when the film is heated in presence of water for a longer period to convert all the barium fluoride [Fig. 2(b)]. The superconducting grains in this case grow as needles and platelets





This anote is copyrighted as indicated in the anticle. Reuse of AIP content is subject to the terms at: http://scitation.alp.org/termsconditions. Downloaded to IP: 147 226 7 162 On: Thit 20 Nov 2014 15:57:21 which are randomly oriented. The results obtained using (100) oriented and randomly oriented YSZ substrates were very similar, suggesting that texturing of the film is not related to substrate orientation alone.

For measuring the resistivity of the films as a function of temperature, a continuous flow cryostat with temperature controller was used. The details of the sample preparation and measurement have been described in an earlier publication.³ A temperature-calibrated silicon diode (+0.1 K)was mounted next to the sample for accurate temperature measurement. Figure 3 shows the normalized resistivity in the transition region of the three films whose x-ray patterns were shown in Fig. 1. Films produced using both procedures, which are preferentially oriented and contain BaF, have an extremely sharp resistive transition with zero resistance obtained at 92-94 K and 10-90% transition width of 1.5-1.7 K [Figs. 3(a) and 3(b)]. On the other hand, when the films are reacted for a longer period to convert all the BaF₂, a broader transition is observed with zero resistance obtained at 85 K [Fig. 3(c)]. We have also measured the resistivity of films which are heated only to 850 °C without annealing at the higher temperature. The room-temperature resistivity of these films is comparable to the above films. They, however, exhibit a much broader transition with zero resistance at temperatures around 77 K. The above results have been consistently reproduced for a number of films which have been prepared to date. It is observed in Fig. 3 that the superconducting transition gets sharper with larger drop in resistivity between room temperature and the superconducting onset temperature, similar to what has been observed by other investigators. The critical current density of films with T_c (R = 0) higher than 90 K is about 1000 A/ cm² at 77 K, whereas films with broader transition, which are also less textured, have critical current density which is an order of magnitude lower.

The superior properties obtained using fluoride precursors are consistent with results obtained by Mankiewich et al. for films deposited by coevaporation on SrTiO₃ substrates using BaF₂ instead of Ba.⁵ Our results suggest that a sharp transition with zero-resistance temperature higher than 90 K is obtained only when some of the fluoride, present as BaF₂, is left unreacted. The BaF₂ certainly helps in preferentially orienting the superconducting phase. It is interesting to note that a sharp transition is observed in these films in spite of presence of secondary phases, unlike films prepared from metal or oxide sources. A possible reason for the improved properties could be fluorine substitution in the superconducting phase, although we do not have any evidence at present to substantiate it. An earlier claim of superconductivity in fluorine-substituted bulk samples of Y-Ba-Cu oxide at temperatures as high as 155 K by Ovshinsky et al.⁷ has been largely discounted by a number of recent publications.⁸⁻¹⁰ There is, however, some evidence that low-level fluorine substitution in bulk samples does sharpen the transition and increases the T_c (R = 0) to 93 K,¹⁰ which is very similar to our results.

In summary, we have demonstrated the use of a new spin-on solution precursor to produce superconducting Y-Ba-Cu oxide films on YSZ substrates which show very sharp



FIG. 3. Normalized resistivity vs temperature for three films whose x-ray patterns are shown in Fig. 1.

resistive transition with zero resistance at temperatures higher than 90 K. The superconducting phase is formed from fluoride intermediates which are converted to the oxides by reaction with water vapor. Preferential orientation of the film, with the c axis normal to the substrate, and a sharp transition is observed only when some of the fluoride phase is left unreacted. We are presently studying the properties of the films by systematically varying the fluorine concentration.

We thank R. H. Koch and R. B. Laibowitz for confirming the resistivity measurements of one of our samples, P. J. Bailey for the scanning electron micrographs, B. L. Olson for the composition analysis, and C. Guerci for technical assistance. We are also grateful to L. T. Romankiw, C. Y. Ting, and Y. Tomkiewicz for helpful discussions, encouragement, and support. The YSZ substrates were made from boules grown by the Ceres Corp., North Billerica, MA.

For example, see papers in *Thin Film Processing and Characterization of High-Temperature Superconductors*, edited by J. M. E. Harper, R. J. Colton, and L. C. Feldman, American Vacuum Society Series No. 3, American Physical Society Proceedings No. 165 (AIP, New York, 1988).

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