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Y-Ba-Cu-O films by rf magnetron sputtering using single composite targets: Superconducting and structural properties

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Y-Ba-Cu-O films by rf magnetron sputtering using single composite targets: Superconducting and structural properties

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High T_c superconducting Y-Ba-Cu-O films have been produced by rf magnetron sputtering using single unreacted composite targets of Y_2O_3, BaF_2, and CuO powders. Transport measurements of the films showed a sharp resistive T_c ($R = 0$) at 89 K and a metallic behavior of resistivity versus temperature. The films show preferred orientations when deposited on single-crystal $SrTiO_3$ substrates (100) or (110) and followed by a post O_2 annealing at 825 °C.

Sputter deposition is one of the most common thin-film fabrication methods used in both basic research and large-scale industrial applications. Recently various sputtering techniques have been employed to produce thin films of the high T_c (90 K) superconducting oxide of $(RE)_1Ba_2Cu_3O_7$[1-7]; these include dc or rf diode or magnetron sputtering under pure Ar or Ar/O_2 atmosphere using single or multiple targets. For preparing these superconducting films, targets used thus far are either oxides or metal alloys (or elements). Furthermore, the substrate temperatures have been found to affect the phase formation, initial stoichiometry, initial distribution of the sputtered species, and film morphology.

In this letter, we report the results of the rf magnetron sputtered films by using unreacted, composite insulating targets made up of Y_2O_3, BaF_2,[8] and CuO. The target compositions have been adjusted to give an optimized film composition in order to obtain the desirable superconducting and structural properties for each specific sputtering and heat treatment condition. Films deposited on single crystals of $SrTiO_3$ with (100) and (110) orientations were found to exhibit strong textures. Uniform films with a T_c ($R = 0$) at 89 K and a metallic behavior of resistivity versus temperature have been obtained.

Previously in our laboratory, superconducting Y-Ba-Cu-O films with T_c ($R = 0$) at 60–70 K have been prepared by both dc diode and magnetron sputtering. Films with T_c ($R = 0$) above 85 K were also occasionally obtained.[1] For these sputtered films, the dependence of resistivity on temperature does not follow the metallic behavior. The resistivity ratios, $\rho(300\ \mathrm{K})/\rho(T_c\ \mathrm{onset})$, are generally around 1.0 or less. In this earlier work, we used conducting targets with compositions close to $Y_1Ba_2Cu_3O_7$.

Among the parameters to improve the superconducting properties, clearly correct film stoichiometry should be the first and the most important requirement. Attempts to adjust the film compositions using the above method of dc sputtering with conducting and fully reacted oxide targets proved to be unsatisfactory. Some of the problems are: (i) The film composition cannot be adjusted by corresponding changes in target composition. According to the ternary phase diagram[9] of Y_2O_3, CuO, and BaO, the phases surrounding the 90 K $Y_1Ba_2Cu_3O_7$ orthorhombic (1:2:3) phase are either semiconducting or insulating. When the target composition deviates from the 1:2:3 composition, it contains several nonconducting phases. dc diode or magnetron sputtering can only be used to sputter conducting or semiconducting (such as CuO) regions of the targets. As a consequence, the film composition cannot be adjusted by the target composition accordingly. (ii) The compacted and sintered oxide powder is not as good a thermal conductor as metal elements such as Cu or Nb. The sluggish heat dissipation occurring inside the target, especially with high-power sputtering, often causes segregation of Ba in the target. Consequently, the chemical composition distribution becomes macroscopically inhomogeneous after repeatedly sputtering depositions. This also contributes to the inconsistency of film fabrication. (iii) The bombardment or sputtering of the films by the negative ions from the target could also be a source of problem in achieving correct film composition and film uniformity.

Superconducting films have also been prepared using a three-gun cosputtering.[7] This method has produced an array of films with a phase spread in which a few films with compositions close to correct stoichiometry do exhibit good superconducting properties. This type of approach is appropriate for the initial phase of study in searching for the optimal film compositions. However, for large-scale applications, methods based on single targets are preferred, when considering film uniformity and the difficulty of precise control of the deposition rates from three separate sources.

Understanding the shortcomings of our previous method[1] and further recognizing the advantages of a single composite target, we have investigated the use of rf magnetron sputtering with unreactive, insulating composite targets. The magnetron gun used in this work is the same as in Ref. 1. The use of the unreactive composite targets of Y_2O_3, BaF_2, and CuO minimizes the macroscopic segregation of Ba in the target, possibly due to a stronger bonding of Ba in BaF_2 than that in the 1:2:3 phase. We have found that a more predictable film composition can now be produced from the new composite targets consisting of oxides and fluoride. Furthermore, the film composition can be adjusted following the target composition.

Pure Ar sputtering was used, with the pressure kept at 6 mTorr during deposition. The substrate-target distance was chosen to be 5 cm. The deposition rate is about 0.1 nm/s. The sputtering targets were cold pressed into disk-shape plates

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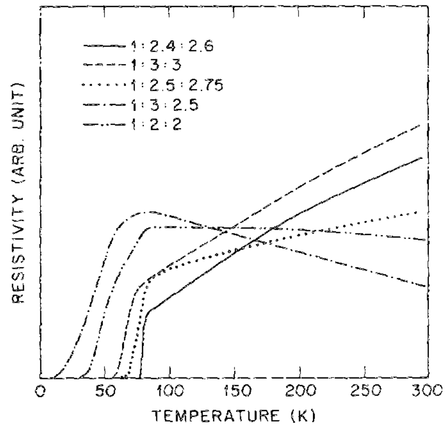

FIG. 1. Resistivity vs temperature of rf magnetron sputtered films from various targets deposited at room temperature and heat treated at 825 °C.

(5 cm in diameter) under a pressure of 1 ton/cm^2. The film composition was examined by Rutherford backscattering spectrometry (RBS). The structure characteristics were studied by x-ray diffraction and transmission electron microscopy (TEM). The superconducting properties were measured using a dc four-point resistance method with an applied current in the range of 2.5–100 μA.

The as-deposited films show uniformly distributed amorphous and/or microcrystalline regions as revealed by scanning electron microscopy (SEM), and x-ray diffraction. The RBS data show the in-depth uniformity in the film composition. The existence of microcrystalline BaF_2 in the as-deposited state is evident from the broad peak in the x-ray diffraction patterns. The films at this stage are insulating, and require post O_2 annealing to become superconducting. Various heat treatments have been tried. Here we report the results from the films annealed at 825 °C for a few hours and followed by a slow furnace cooling.

Several films deposited from targets with different compositions have been obtained and the transport measurements for the annealed films are shown in Fig. 1. Here and what follows, we designate symbols such as 1:3:3 to represent the atomic ratios of $1\times 1/2$ Y_2O_3:$3\times BaF_2$:$3\times CuO$ in the target. In addition, the 1:3:3 film denotes the film sputtered from the 1:3:3 target. Films deposited from the 1:3:3 target may have different compositional ratios. The sputtering conditions and the post oxygen annealing treatments were kept the same for all the films described in Fig. 1. The substrate temperature for these films was kept at room temperature. For the 1:3:2.5 and 1:2:2 films, the resistance versus temperature (R vs T) curves show a negative slope. Also T_c ($R=0$) values are below 50 K.

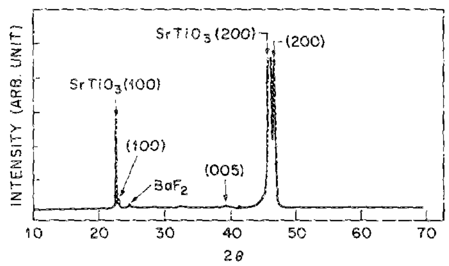

FIG. 3. X-ray diffraction pattern of a rf magnetron sputtered film of $Y_1Ba_2Cu_3O_7$ on $SrTiO_3$ (100).

For the 1:3:3, 1:2.5:2.5, and 1:2.4:2.6 films, we have observed not only a positive slope in the R vs T curves but also a systematic increase of T_c ($R=0$) at 60, 68, and 78 K, respectively. In contrast with our earlier approach,[1] we have rarely obtained films with a positive slope in the R vs T data. Films deposited at room temperature with T_c ($R=0$) between 70 and 80 K have been consistently obtained using targets with compositions around 1:2.4:2.6 and a heat treatment at 825 °C. The room-temperature resistivity values for the films in Fig. 1 are in the range of 1000–2000 $\mu\Omega$ cm. These values are higher than those obtained for the molecular beam epitaxy (MBE) grown epitaxial films (350 $\mu\Omega$ cm).[10] This is probably attributed to the existence of multiple phases and microcracks in the sputtered films.

We have studied the superconducting and structural properties of sputtered films obtained from ten different targets with substrates kept at room temperature during film deposition. The difficulty of obtaining a T_c ($R=0$) higher than 80 K is very likely due to the initial distribution of the sputtered species. For all the films deposited at room temperature, the x-ray diffraction data show strong BaF_2 peaks. We have also found that the intensity of the BaF_2 peaks in the as-deposited films decreases with increasing substrate temperature. This indicates a diminishing amount of BaF_2 microcrystals, thus providing a better initial distribution of sputtered species for the films prepared at higher temperatures. Along this direction, several films were prepared with a 450 °C substrate temperature. The as-deposited films are still insulating. However, with a post O_2 annealing at 825 °C for 4–10 h, the films exhibit a T_c ($R=0$) at 89 K with a

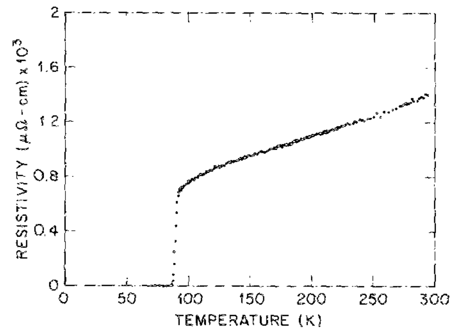

FIG. 2. Resistivity vs temperature of rf magnetron sputtered film deposited at 450 °C and heat treated at 825 °C.

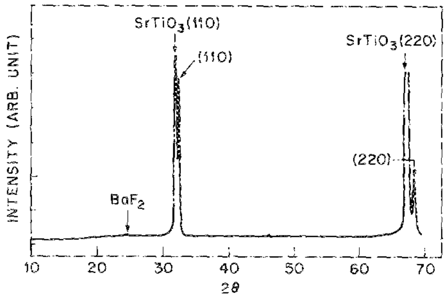

FIG. 4. X-ray diffraction pattern of a rf magnetron sputtered film of $Y_1Ba_2Cu_3O_7$ on $SrTiO_3$ (110).

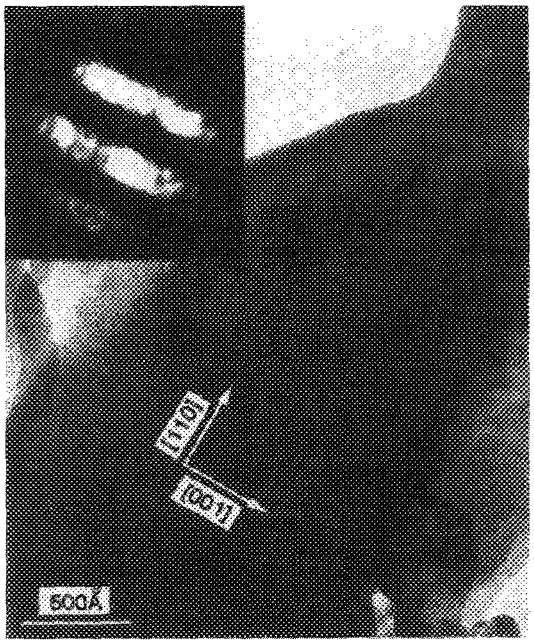

FIG. 5. Transmission electron micrograph and electron diffraction of the same film as in Fig. 4.

metallic R vs T curve (see Fig. 2). The resistivity ratio of $\rho(300\ \text{K})/\rho(T_c\ \text{onset})$ is 2.0.

Previously, our dc diode or magnetron sputtered films deposited on Al_2O_3, MgO, or $SrTiO_3$ substrates showed random orientations when annealed at temperatures below 900 °C. The films deposited on $SrTiO_3$ (100) began to show preferred orientations with c axis perpendicular to the film surface when the annealing temperature exceeded 950 °C.[11] This is expected based on the partial melting region in the ternary phase diagram.[9] The 1:2:3 superconducting phase was found to grow in rectangular platelets with sizes around $200 \times 50\ \mu\text{m}$ in a film annealed at 1040 °C. Each platelet is a single crystal and was found to be epitaxially aligned with the substrate with c axis perpendicular to the film.[11]

For our new sputtered films on single-crystal $SrTiO_3$ substrates, preferred orientations were also observed by x-ray diffraction and TEM. These oriented films were obtained with post O_2 annealing at 825 °C. For films deposited on $SrTiO_3$ (100), we have observed predominantly the a axis perpendicular to the film plane as shown in Fig. 3. For films deposited on $SrTiO_3$ (110), a (110) orientation of $Y_1Ba_2Cu_3O_7$ has been found to be normal to the film surface as evidenced from the x-ray diffraction in Fig. 4. The structural characteristics of the films on $SrTiO_3$ (110) were further studied by TEM which showed a distribution of grains with the in-plane axes $\hat{c}$ and $\langle 1\bar{1}0\rangle$ preferentially aligned (Fig. 5). In these films, the shape of the superconducting $Y_1Ba_2Cu_3O_7$ grains is needle-like, and c axis along with the short edge and $\langle 1\bar{1}0\rangle$ parallel to the longer side. The c axis and $\langle 1\bar{1}0\rangle$ of the films are aligned with the $\langle 001\rangle$ and $\langle 1\bar{1}0\rangle$ of $SrTiO_3$, respectively.

In conclusion, we have produced high T_c superconducting oxide films in the Y-Ba-Cu-O system by rf magnetron sputtering using insulating, unreacted, composite single targets of Y_2O_3, BaF_2, and CuO. Films with T_c ($R = 0$) at 89 K and a metallic behavior in resistivity versus temperature have been obtained. Film compositions are more controllable by the present sputtering approach than by the previous method using conducting targets with compositions near $Y_1Ba_2Cu_3O_7$. With heat treatments at 825 °C in O_2, the present films, deposited on $SrTiO_3$ single-crystal substrates show preferred orientations, as revealed by x-ray diffraction and TEM studies. Furthermore, for films on $SrTiO_3$ (110) the TEM results show a distribution of grains with in-plane axes $\hat{c}$ and $\langle 1\bar{1}0\rangle$ aligned.

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