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$_2$O$_3$, 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)$_2$Ba$_2$CuO$_y$; 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$_2$O$_3$, BaF$_2$, 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. For these sputtered films, the dependence of resistivity on temperature does not follow the metallic behavior. The resistivity ratios, $\rho(300 \, K)/\rho(T_c \, onset)$, are generally around 1.0 or less. In this earlier work, we used conducting targets with compositions close to Y$_1$Ba$_2$Cu$_3$O$_7$.

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$^7$ of Y$_2$O$_3$, CuO, and BaO, the phases surrounding the 90 K Y$_1$Ba$_2$Cu$_3$O$_7$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.$^8$ 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 methods$^4$ 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$_2$O$_3$, 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.
The superconducting properties studied and require applied current in diffraction patterns. The 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 of the target may have been influenced by the target. In addition, the 1:3:3 target was obtained and the atomic ratios of the films annealed at 825°C 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 μΩ cm. These values are higher than those obtained for the molecular beam epitaxy (MBE) grown epitaxial films (350 μΩ cm). 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 transition temperature above 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 BaF2 peaks. We have also found that the intensity of the BaF2 peaks in the as-deposited films decreases with increasing substrate temperature. This indicates a diminishing amount of BaF2 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 O2 annealing at 825°C for 4–10 h, the films exhibit a transition temperature above 80 K with a
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$_2$O$_3$, 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 x 50 μm 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 $Y_1$Ba$_2$Cu$_3$O$_7$ 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 (110) preferentially aligned (Fig. 5). In these films, the shape of the superconducting $Y_1$Ba$_2$Cu$_3$O$_7$ grains is needle-like, and $c$ axis along with the short edge and (110) parallel to the longer side. The $c$ axis and (110) of the films are aligned with the (001) and (110) 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 $Y_2$O$_3$, 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 $Y_1$Ba$_2$Cu$_3$O$_7$. 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 (110) aligned.
