

Preparation of Superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ Thin Films by RF Magnetron Sputtering

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Abstract

Superconducting thin films of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ were deposited in situ on MgO (100) substrates heated at 700°C, using the single target 90° off-axis RF magnetron sputtering. The films were grown with the c-axis perpendicular to the film plane. The superconducting transition temperature of the deposited films was 83.2 K. The origin of the degradation of T_c in thin films was discussed.

1. Introduction

The discovery of high T_c (transition temperature) superconducting cuprates with $T_c > 77$ K (liquid N_2 temperature), such as $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ (YBCO, $T_c = 92$ K)¹⁾ immediately triggered interest to prepare them as thin films. These materials should greatly simplify the use of superconducting electronic systems and thereby increase their range of application in the liquid N_2 temperature. For electronic application, they must be fabricated in thin films. Main methods to deposit hetero-epitaxial superconducting thin films on substrates were laser ablation²⁾, multi-source electron-beam thermal evaporation³⁾, single-target DC or RF magnetron sputtering⁴⁾, metal-organic chemical vapor deposition⁵⁾ and molecular beam epitaxy⁶⁾. Among these deposition methods, single-target magnetron sputtering can be a very reproducible and easily controllable technique. Usually argon gas is used for sputtering gas, but oxygen as a reactive component has to be mixed with the argon for the high T_c superconducting oxides. Bulk YBCO ceramics are used for targets. Typical substrates are single crystals of MgO, SrTiO_3 and LaAlO_3 . The bias voltage between an anode (substrate) and a cathode (target) ionizes argon atoms and accelerates them towards the target, sputtering of YBCO molecules towards the substrate, and the thin film of YBCO is deposited on the substrate.

There are two generic approaches to thin film growth that can produce YBCO films. The first is the so-called post-annealed approach, in which the YBCO thin film is deposited on the substrate at an ambient temperature as an amorphous or disordered mixture and then subsequently heat-treated at about 850°C in oxygen atmosphere to react the constituents and to form the YBCO crystal structure⁷⁾. This approach has drawbacks. It is limited in the choice of substrates with which it can be used, as it involves high processing temperatures. The resultant films are not single crystals, and they have relatively rough surfaces.

The second is the in situ approach, in which the YBCO crystal structure is grown on the

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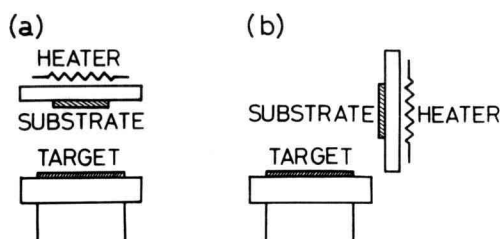


Fig. 1. Single target sputtering configurations. (a) on-axis. (b) off-axis.

heated substrate during the deposition process. For an MgO (100) substrate, *c*-axis of YBCO is grown along the substrate at the substrate temperature between 500°C and 575°C and *c*-axis grown normal to the substrate at the substrate temperature above 600°C⁸⁾. In most cases the substrate is heated at temperatures between 650°C and 750°C, and the deposited films are highly oriented with the *c*-axis normal to the plane. The as-deposited films were oxygen deficient, therefore the films were heat treated at 400–450°C in an oxygen atmosphere after the deposition.

The main problem in the standard sputtering configuration which is called an on-axis sputtering as shown in Fig. 1(a) is that, unlike argon which ionizes only as Ar^+ , oxygen ionizes also as O_2^- and O^- which cause resputtering of the thin film deposited on the substrate and severely change the composition of the film. Several groups^{9,10)} have used non-stoichiometric targets to compensate for the selective resputtering effect. Alternatively, Poppe et al.¹¹⁾ have sputtered a stoichiometric target at high pressure (6 Torr). At this pressure, the mean free path of the negative ions is a few microns, and they will lose their energy when reaching the substrate. The uniformity of the resulting film is usually poor. Instead of a planar geometry, Various groups^{12,13)} have used an off-axis sputtering as shown in Fig. 1(b), in which substrates are placed on the side of the target, to avoid resputtering damage from negative oxygen ions. They have successfully made in situ YBCO films by the off-axis configuration. The T_c of these in situ films were from 75 to 89 K. Though the superconducting transition was sharp in these films, the T_c was slightly lower than that of the bulk YBCO ceramics.

In this paper, we fabricate superconducting YBCO thin films using the off-axis single-target RF magnetron sputtering. Properties of the deposited thin films are examined by electrical resistivity, X-ray diffraction and scanning electron microscopy, and compared to that of bulk ceramics. We discuss the origin of the degradation of T_c in thin films.

2. Experimental

We have used the off-axis sputtering geometry. Substrates were positioned perpendicular to a target surface. In this configuration, if one drew a line normal to the center of the target and another line normal to the center of the substrate holder, the intersection of these lines would be 6 cm from the substrate holder and 4 cm from the target surface. When we

placed the substrates 5 cm away from the target in the on-axis configuration and the substrates were heated at around 650°C, nothing was deposited on the substrates due to the resputtering of oxygen ions. When we replaced the substrates 3 cm away from the target in the on-axis configuration, surfaces of the deposited films were rough and the composition of the film was severely poor in Ba and Cu. However, by going to the 90° off-axis geometry, high quality films could be repeatedly obtained.

Stoichiometric YBCO targets were prepared by solid state reaction. A powder of reagent grade Y_2O_3 , BaCO_3 and CuO was weighted in a molar ratio of $\text{Y} : \text{Ba} : \text{Cu} = 1 : 2 : 3$, crushed and mixed with a mortar and pestle. The mixed powder was placed in alumina crucibles and calcined at 850°C for 12 hr. The calcined powder was pulverized and calcined again at 850°C for 6 hr. The calcined powder was pulverized and poured into a die and pressed into a pellet. The pellet was sintered at 950°C for 6 hr and annealed at 450°C for 12 hr, in a flowing oxygen atmosphere. The size of the annealed pellet was 48 mm in diameter and 4 mm in thickness.

Initially, an RF power of 100 W was supplied to a magnetron sputter source (Lesker TRS-002C), then the target cracked due to thermal stress. When the RF power was reduced to 50 W, the target did not cracked. The RF power level was always fixed to 50 W in the sputtering process.

MgO (100) single crystals were used for substrates. Their size was 10 mm × 10 mm × 1 mm. As polished surfaces of MgO were rough in an atomic scale, in situ films were amorphous or disordered. Before the deposition, MgO substrates were annealed in a flowing oxygen atmosphere at 950°C. The substrates were bonded by silver paste to a substrate holder. The temperature of the substrate holder was measured by an alumel-chromel thermocouple, and was held constant at 700°C during film growth. The actual substrate surface temperature was somewhat lower than that of the substrate holder.

The sputtering atmosphere which was measured by Schultz gauge was varied between 1–3 Pa O_2 and 1–5 Pa Ar. Glow discharge stopped at a lower sputtering atmosphere of 1 Pa, and the deposition rate reduced severely at a higher sputtering atmosphere of 10 Pa due to collisions with a sputtering gas. As the deposited films were oxygen deficient, the films were annealed at 450°C in 1 atm of oxygen after the deposition.

Resistance measurements were performed using the AC four point method with contacts prepared by silver paste. The temperature of the thin films was measured by an $\text{Au} + 0.07\%$ Fe-chromel thermocouple. An X-ray diffraction analysis was done using RIGAKU RAD-C diffractometer using $\text{CuK}\alpha$ radiation. The compositions of thin films were determined by energy dispersive x-ray analysis (EDX) with JEOL JXA 840A scanning electron microscope. Polished $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ bulk ceramics were used as standards.

3. Results and Discussion

As an example, we show in Fig. 2 the temperature dependence of resistance of the YBCO thin film which is deposited in a sputtering atmosphere of 4 Pa (50% Ar/50% O_2) for 5 hr.

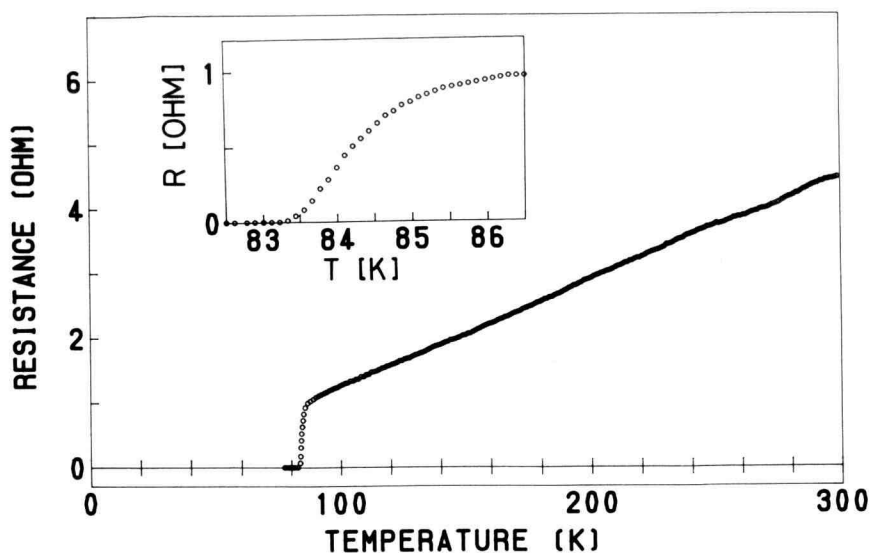


Fig. 2. Typical temperature dependence of resistance of a thin film deposited on MgO. An inset shows the temperature dependence of the resistance of the film near the transition temperature.

This film is shining and smooth. The optimum sputtering condition is now under way. The resistance of this film is metallic and the transition temperature for zero resistance is 83.2 K. Although the transition temperature is lower than that of the bulk ceramics, the transition width is narrow.

In Fig. 3, we show the X-ray diffraction spectrum of this film. The diffraction peak marked as "MgO (200) $\text{CuK}\beta$ " at 38.6° is due to the MgO substrate by $\text{CuK}\beta$ radiation. The peaks at 42.8° and 43.1° are also due to MgO substrate by $\text{CuK}\alpha$ radiation. The other peaks can be indexed as from (001) to (007). The data shown here reveal that the film is grown with the c-axis perpendicular to the film plane. The c-axis lattice parameter of this film is calculated to be 1.179 nm. The c-axis lattice parameters vary with the sputtering conditions, and there is a tendency that the transition temperature increases with decreasing the c-axis lattice parameter. The crystal structure of bulk $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ ceramics is orthorhombic for $y < 0.5$, and tetragonal for $y > 0.5$. In the orthorhombic phase, YBCO is superconductive and lattice parameters are $a = 0.388$, $b = 0.382$ and $c = 1.169 \text{ nm}^{14}$. In the tetragonal phase, YBCO is semiconductive and lattice parameters are $a = 0.386$ and $c = 1.178 \text{ nm}^{14}$. The c-axis lattice parameter of this film is larger than that of the tetragonal phase in bulk YBCO ceramics. The resistance of this film is not semiconductive, but metallic. In Y-Ba-Cu-O system, superconductive $\text{YBa}_2\text{Cu}_3\text{O}_{8-y}$ ($T_c = 81 \text{ K}$) and $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15-y}$ ($T_c = 70 \text{ K}$) are also synthesized¹⁵. Their c-axis lattice parameters are 1.360 and 1.255 nm, respectively, and both are much larger than that of this film. Eom et al.¹³ reported that the c-axis lattice parameter of in situ films deposited by sputtering increases with decreasing substrate temperature and with decreasing oxygen pressure, and varied from 1.167 to 1.182 nm. The c-axis

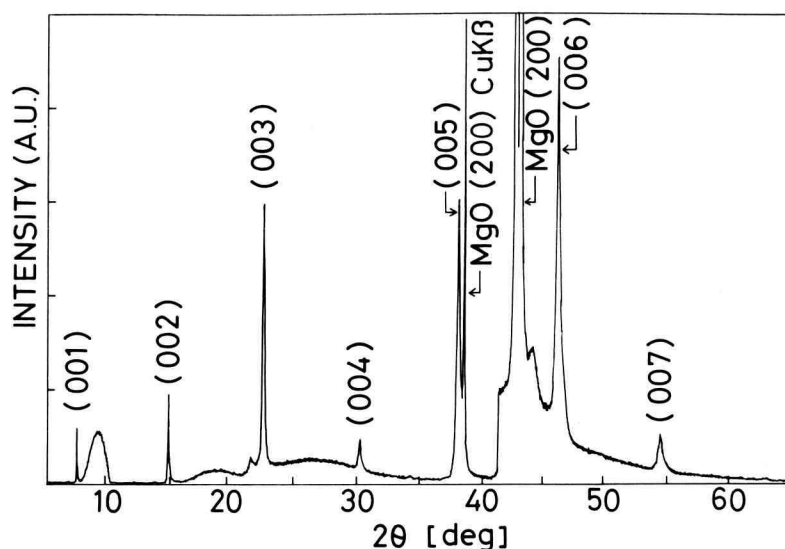


Fig. 3. X-ray diffraction pattern of the thin film using $\text{CuK}\alpha$ source. Peaks labeled "MgO (200) $\text{CuK}\beta$ " and "MgO (200)" are due to MgO substrate.

lattice parameter of this film is in this range. The crystal structure of this film is thus assigned as $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$. As the thin films have been annealed at 450°C in 1 atm oxygen atmosphere, the expansion of the c -axis lattice parameter is not due to oxygen deficiency in the chain site, as is the case for bulk ceramics. It is rather possible that the low-temperature growth of thin films introduces disorder or defects. Such defects on the oxygen "bridge" sites, for example, could account for the increased c -lattice parameter.

The composition of the film is measured by EDX. The composition of the film is $\text{Y} = 0.176$, $\text{Ba} = 0.311$ and $\text{Cu} = 0.513$. The relative atomic ratios of Ba/Y and Cu/Y are 1.77 and 2.91, respectively. The stoichiometric $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ would have the relative atomic ratios of $\text{Ba}/\text{Y} = 2.00$ and $\text{Cu}/\text{Y} = 3.00$. We see that the film is deficient in Ba and Cu. This film is in part amorphous or disordered. The degradation of T_c of this films may be caused also by the non-stoichiometry.

In $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$, its optimum oxygen content is critical and its phase transformations can introduce undesired defects. It may be necessary to introduce active oxygen such as ozone for easier oxidation.

4. Conclusions

Superconducting thin films of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ were deposited in situ on $\text{MgO}(100)$ substrates using the single target 90° off-axis RF magnetron sputtering. The films were grown with the c -axis perpendicular to the film plane. The transition temperature of the deposited films was 83.2 K. The degradation of T_c in thin films was due to non-stoichiometry and

oxygen-deficiency.

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