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High Tc superconducting oxide films prepared by sputtering

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Abstract - Recent studies on high Tc superconducting oxide films are reviewed with special emphasis on the preparation by sputtering. Comparison and analysis are made on various preparation methods to point out key factors and problems which must be taken into account for the film synthesis. Some experimental details and results are presented with respect to the preparation of La-Sr-Cu-O and Yb-Ba-Cu-O films by 50 Hz ac sputtering in which we observed some features characteristic to the film preparation on ceramic substrates. Epitaxial growth of single crystal Y-Ba-Cu-O films is also noted, since the anisotropic and high critical current density of the films is quite important not only for the application to electronic devices but also for the mechanistic studies of superconductivity.

INTRODUCTION

Recent discoveries of high Tc superconducting oxides such as La-Ba-Cu-O (ref. 1), La-Sr-Cu-O (ref. 2), and Y-Ba-Cu-O (ref. 3), triggered the extensive studies on the preparation of thin films of these oxides, since electronic devices using these superconductors can be practically very important in the near future and most of them will be fabricated by cumulating thin films on insulating substrates. Among various methods so far reported for the synthesis of superconducting oxide films, there are two methods which include plasma processes : sputtering and plasma spray. The former uses low temperature plasma, while the latter high temperature plasma. Since the sputtering was already proved to be useful for depositing films of various ceramics including $Ba(Pb,Bi)O_3$, a previously known perovskite type superconductor (ref. 4), it is considered to be one of the most promising techniques for the film deposition of high Tc superconducting oxides which also have perovskite-like structures.

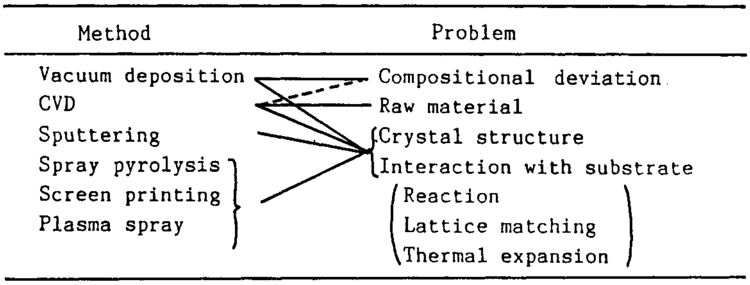
Here, I would like first to summerize the recent progress in the superconducting film preparation and then to specify the factors crucially important for the realization of superconductivity in the sputter-deposited films. Experimental evidences are primarily cited from our results on the preparation of La-Sr-Cu-O (ref. 5 - 7) and Yb-Ba-Cu-O (ref. 8 & 9) films by using a simple ac sputtering apparatus. Also described are the sputtering conditions and properties of films reported by other research groups. Included is the epitaxial growth of single crystal films on single crystal $SrTiO_3$ substrates (ref. 10). Discussion will be extended to preliminary results of the device application and microprocessing of superconducting thin films.

FILM PREPARATION METHODS AND PROBLEMS

Table 1 shows the methods and problems which could be generally applied to the film synthesis of multi-components compounds on substrates. Thin films of both K_2NiF_4 type 40K class and oxygen-deficient perovskite type 90K class superconducting oxides have been prepared by vacuum evaporation and sputtering. Electron beam evaporation was used by two groups in USA to produce thin films exhibiting zero resistivity temperature(Tc) and critical current (Jc) values in excess of 80K and $10^5 Acm^{-2}$ at 77K, respectively (ref. 11 & 12). As will be described in more detail later, sputtering has been confirmed by several research groups in Japan, China, Europe and USA to be an equally good or even better method for the preparation of high Tc oxide films. The films as-deposited in these vacuum techniques are usually semiconducting and post annealing in oxygen or in air at elevated temperatures is necessary for making the films superconducting.

Although chemical vapor deposition (CVD) is considered to be a good method because of its probable high productivity, source gases, especially of alkaline earth metal component, are obviously the weak point of the method at present. Spray pyrolysis (ref. 13) and other techniques such as screen printing (ref. 14 & 15) and plasma spray were successfully applied to prepare films relatively thicker than those deposited in vacuum chambers.

Table 1 Methods and problems of the preparation of superconducting oxide films.



Method	Problem
Vacuum deposition	Compositional deviation
CVD	Raw material
Sputtering	Crystal structure
Spray pyrolysis	Interaction with substrate
Screen printing	Reaction
Plasma spray	Lattice matching
	Thermal expansion

The primary requirement for getting superconducting films is the compositional adjustment; film composition must be almost the same as the optimum composition of bulk superconductor. Since the compositional deviation from evaporation source or sputtering target is frequentry observed in evaporation or sputtering of alloys or composites, the metallic composition of films deposited by these methods should be analyzed by such a method as ICP (inductively coupled plasma) emission analysis or EPMA (electron probe micro analysis). The optimum deposition conditions and the appropriate source or target composition could be estimated by accumulating analytical data on numerous samples. The oxygen composition, i.e. the nonstoichiometry δ in $(La_{1-x}Sr_x)_2CuO_{4-\delta}$ and $YBa_2Cu_3O_{7-\delta}$, which is found to be crucially important for the superconductivity, is controlled by the annealing and quenching conditions (ref. 16).

The second requirement is the control of crystal structure. The substrate temperature at the film deposition as well as the annealing condition gives dominent effect on this problem.

The third and most substantial problem in the film preparation is the interaction of oxide film with substrate. Chemical reactions during the deposition and/or annealing, the lattice matching, and the difference in thermal expansion coefficient between the films and substrates should consist of this probrem.

FILM PREPARATION BY AC SPUTTERING

Although the preparation of bulk samples of high Tc superconducting oxides is no longer so difficult, there have appeared still limited numbers of successful studies of thin film deposition. Main difficulties are presumed to come from the problems described above. We have found some typical examples clearly indicating these problems through our studies on the preparation of superconducting La-Sr-Cu-O and Yb-Ba-Cu-O films. The films were first prepared in February and March of this year, respectively.

Experimental

Among various types of sputtering appratus, we employed a very simple ac sputtering system, which we designed ourselves, primarily because of the experimental convenience. Figure 1 represents schematically the 50 Hz ac sputtering and heating system we used for the deposition of films. In the reacter of quartz cylinder (5cm Φ x 50cm), a pair of disk targets (2cm Φ x 3mm each) are mounted on the copper rods inserted horizontally and they are used simultaneously as electrodes. The targets are sputtered by the application of 50Hz ac high voltage ($\sim$6kV). The film is deposited on a substrate placed at the bottom of the reactor. The substrate temperature ($\lesssim$700 °C)and the total pressure of the system (10-170mTorr) are regulated to be constant throughout the sputtering by introducing an appropriate amount of sputtering gas.

The La-Sr-Cu-O and Yb-Ba-Cu-O superconducting powders are prepared by the powder mixing and calcining method. The calcined powder is pressed into the disks. Corning #7059 glass, quartz, alumina, sapphire, and yttria stabilized zirconia (YSZ) are used as substrates. Resistivities of the films deposited on these substrates are measured by the dc four probe methods. Metal composition and crystal structures of the films are analyzed by an ICP emission analyzer (Jarrel Ash Atom Comp MK II) and X-ray diffractometer (Rigakudenki RAD-2C), respectively. The surface and cross section of the films are observed by a scanning electron microscope (Hitachi S-800).

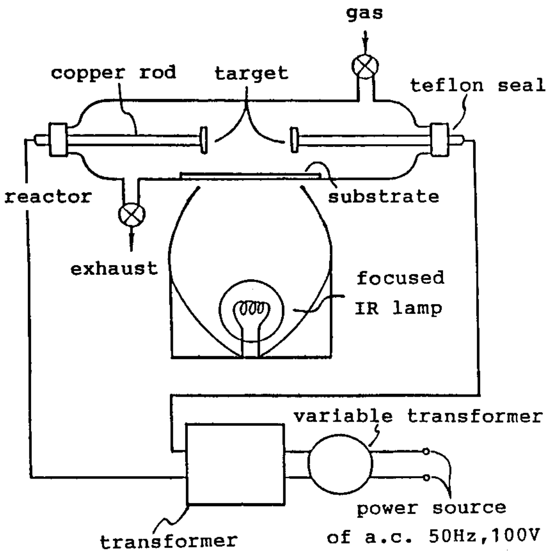


Fig. 1 Schematic representation of ac sputtering apparatus.

Results and discussion

Figure 2 shows the sputtering gas dependence of the analysed metal composition,x and y in $(Yb_{1-x}Ba_x)_yCuO_{3-\delta}$, of the films prepared by the sputtering of a pair of targets having a nominal composition of $Yb_{0.25}Ba_{0.75}CuO_{3-\delta}$. Sputtering time for all the films was about 5h and typical thickness of the obtained films was 0.5 μm. The metal composition was quite sensitive to the sputtering gas ratio $(O_2/(Ar+O_2))$; the film compositions turned out to be nearly the optimum Yb/Ba/Cu = 1/2/3 ratio at the gas ratios ranging from 0.1 to 0.3. The film composition was also affected by the substrate temperature to some extent. As shown in Fig. 3, at temperatures higher than 500°C,the film composition deviated from target composition, probably due to the evaporation of CuO.

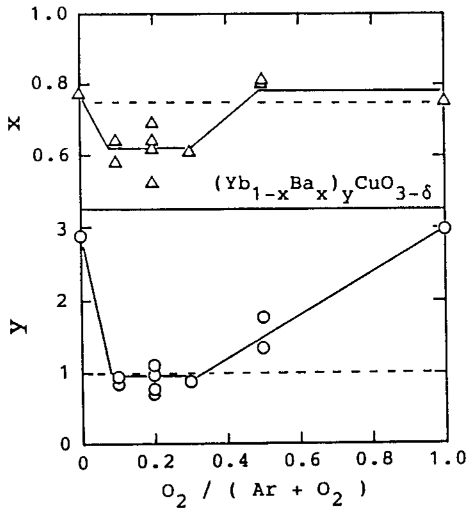


Fig. 2 The dependences of the film compositions on the sputtering gas mixing ratio $(O_2/Ar+O_2)$. The dashed lines indicate target compositions. The optimum Yb/Ba/Cu=1/2/3 ratio corresponds to x=0.67 and y=1.0

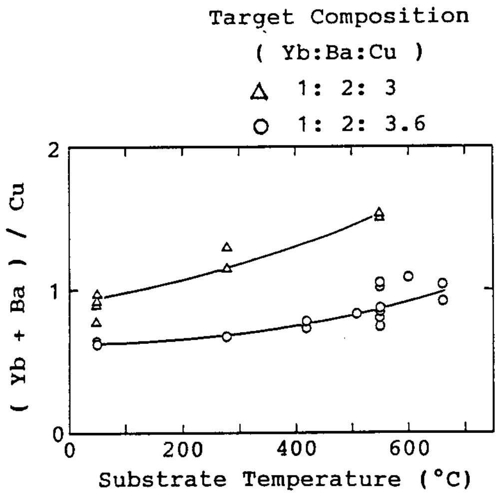


Fig. 3 The dependence of the films composition ((Yb+Ba)/Cu) on the substrate temperature.

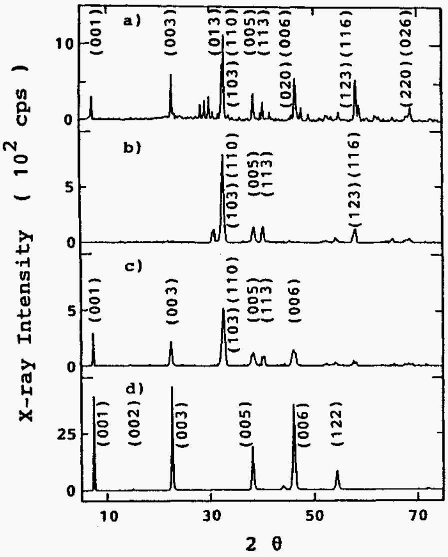


Fig. 4 X-ray (Cu-K_α) diffraction patterns of Yb-Ba-Cu-O as-deposited films on YSZ substrates at various substrate temperatures (T_s). (a): the pattern of $YbBa_2Cu_3O_{7-\delta}$ powder, (b): $580 \leq T_s \leq 640$ °C, (c): $640 \leq T_s \leq 650$ °C, (d): $650 \leq T_s \leq 660$ °C. The peaks of substrate at $2\theta = 29$-31°, 49-51°, and 59-61° are omitted from the original pattern.

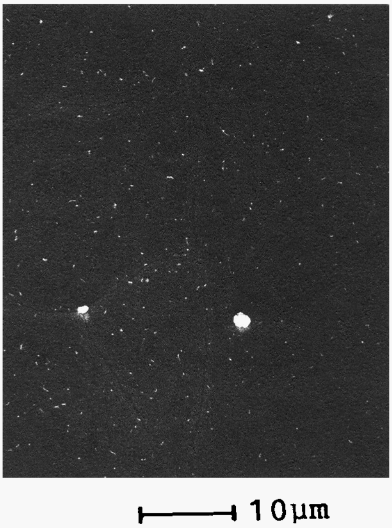


Fig. 5 Scanning electron micrographs of La-Sr-Cu-O film prepared by ac 50Hz sputtering and annealed at 590 °C for 15h. (substrate: Corning #7059 glass)

Figure 4 shows X-ray diffraction patterns of Yb-Ba-Cu-O films prepared under various thermal conditions. In Fig. 4, the peak at $2\theta = 7.6°$ (d=11.7A) is assignable to (001) in tripled cell of $YbBa_2Cu_3O_{7-\delta}$ as it is in the bulk superconducting $YBa_2Cu_3O_{7-\delta}$ (ref. 17). The crystal structure is strongly dependent on the substrate and annealing temperature. In the relatively low temperature range ($580 \leq T_s \leq 640$ °C), the film did not give a diffraction peak at 7.6° as exemplified in Fig. 4(b). Temperatures of this range are presumed to be high enough to crystallize the depositing films into polycrystalline perovskite phase, but not high enough to induce the ordering of A site ions into the Ba-Yb-Ba tripled cell structure. In the films prepared at temperatures of the intermediate range ($640 \leq T_s \leq 650$ °C), the peak at 7.6° came to be seen (Fig. 4(c)). Thus, the crystal structure of film resemble to that of bulk specimen shown in Fig. 4(a). As describe later, the films prepared at temperatures of this range have the highest T_c^{zero} among the films so far prepared. In the temperature range higher than 650°C, the films deposited are estimated to be highly orientated to the (001) direction (Fig. 4(d)) and the A site ions should have the periodical structure of the tripled cell. Although the films had low resistivities in the order of $10^{-3} S^{-1} cm$ when the measurements were carried out soon after the film preparation, they were not so stable in air and frequently changed to be hazy in a few hours. These hazy films were insulators having no sharp peak in their XRD patterns. The films might have reacted with moisture to form amorphous oxyhydrates.

A reaction between the film and substrate was observed clearly when an La-Sr-Cu-O film deposited on quartz substrate was heated up to 1000 °C. The black conductive film turned to be grayish green insulator by the heating. No success has been reported so far on the preparation of high Tc superconducting oxide films on such substrates as silicon wafers and silica glass.

The mismatch of thermal expansion was an unexpectedly big problem ; fine cracks were formed in the whole area of La-Sr-Cu-O film deposited on glass substrate and annealed at 590 °C, as is shown in Fig. 5. Crack formation was also observed on La-Sr-Cu-O film on alumina substrate by quenching the film after heating up to 1000 °C, although high Tc Y-Ba-Cu-O films were reported by other groups to be prepared on alumina and sapphire substrates(see Tab. 2).

The thermal expansion behavior of bulk $(La,Sr)_2CuO_{4-\delta}$ and $YBa_2Cu_3O_{7-\delta}$ were measured. Figure 6 depicts the latter data. Not only the linear thermal expansion coefficient (ca. 1.4×10^{-5} K^{-1}) averaged over the temperature range of 30-900°C is appreciably greater than the values measured for ordinary used ceramic substrates, but also the coefficients for temperature range around the phase transition between orthorhombic and tetragonal are extremely high (ca. 3.3×10^{-5} K^{-1}).

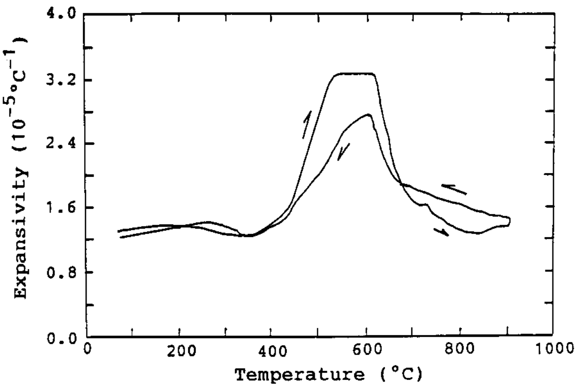


Fig. 6 The temperature dependence of linear thermal coefficient for $YbBa_2Cu_3O_{7-\delta}$ in air.

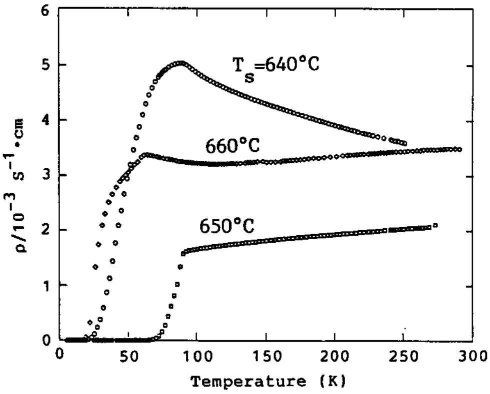


Fig. 7 Resistivity vs. temperature relationship for Yb-Ba-Cu-O film specimens prepared at various substrate temperatures(T_s).

From all these and some other results, such conditions as the following were expected to be desirable for the preparation of high Tc superconducting Yb-Ba-Cu-O and related oxide films without postannealing the films at temperatures higher than the deposition temperature.

1) Target containing Cu in exess (∿20%)
2) Substrate heating at about 650°C
3) Annealing at temperatures of 600-650°C in oxygen atmosphere
4) Chemically inert substrate having relatively large thermal expansion coefficient

Although the optimum preparation conditions should change from a reacter to another, the most significant point is frequent check of film composition and crystal structure so that the preparation parameters could be correlated with the structure.

Figure 7 is examples of resistivitity-temperature relationship measured for Yb-Ba-Cu-O films prepared by ac sputtering on YSZ substrates.

PRESENT STATUS AND FUTURE PROSPECT OF THIN FILM RESEARCH

Table 2 summarizes the reported preparation of high Tc superconducting oxide films by sputtering (ref. 18 - 24). Although no film has Tc values exceeding 95K, i.e. the highest stable Tc reported for bulk superconductors, most of the films have critical current (Jc) values far greater than the values determined for bulk samples. Especially, Enomoto and coworkers recently announced that the single crystal $Ba_2YCu_3O_{7-\delta}$ thin film was grown epitaxially on a single crystal $SrTiO_3$ (110) substrate by magnetron sputtering and that it had high and

Table 2 Preparation of high Tc superconducting oxide films by sputtering.

Sputtering mode	Compound	Conditions			Anneal	Tc	Research	Ref.
		Substrate	Temp.(°C)	Press.(Pa)	(°C,h)	(K)	group	
ac(50Hz)	La-Sr-Cu-O	YSZ	450	7	725,15	17	Tokyo U.	5
"	Yb-Ba-Cu-O	YSZ	650	23	600,0.5	66		8
rf(13.56MHz)	La-Sr-Cu-O	Alumina MgO	680	<7	-	27	ETL	18
dc-magnetron	La-Sr-Cu-O	Sapphire	no heating	-	800,	10	Inst.Phys. China	19
"	Y-Ba-Cu-O	Sapphier	1050	4	500,0.1	36	Cambridge U.	20
rf-magnetron	La-Sr-Cu-O	$SrTiO_3$ (100)	-	-	800,8	15	NTT	21
"	Y-Ba-Cu-O	$SrTiO_3$ (110)	700	11	920,2	84	"	10
"	"	Sapphier (1102)	200	0.4	900,1	70	Matsushita Elec.	22
"	"	$SrTiO_3$ (100)						
"	"	YSZ,MgO $SrTiO_3$	no heating	-	900,2	85	Hitachi	23
"	"	MgO	<700	-	<950,	85	Sumitomo Elec.	24

anisotropic superconductivity. The critical current density along the basal plane of the crystal reached 1.8×10^{6} Acm^{-2} at 77K (ref.10), while the Jc perpendicular to the plane was in the order of $10^{4}Acm^{-2}$. This result provides a convincing support for a quasi two-dimensional electronic structure in this superconductor. Even a polycrystalline film was reported to have a Jc of 3.2×10^{4} Acm^{-2} at 77K (ref. 24). The Meissner effect was observed by Hotta et. al. in Y-Ba-Cu-O films (ref. 25). We also detected diamagnetism in a sputtered La-Sr-Cu-O superconducting film by the measurement of dc susceptibility using SQUID.

Different from bulk superconductors, properties of thin films have been approaching practical level. For device application, lower deposition temperature and as-deposited superconductivity should be strongly preferred. Problems to be solved will include further optimization of preparation conditions to increase Tc and Jc, the acceleration of oxygen incorporation in the film, and the deposition of insulating film which has good compatibility with superconductors. Furthermore, microprocessing of superconducting films is required for device fabrication. Oxygen ion implantation into YBCO film was already used to make a part of the film insulating by Laibowitz et. al. (ref. 11). By combining a pair of weak-link type Josephson Junctions, they fabricated a SQUID which could be operated at temperatures up to 68K. Plasma, laser, and ion processes on superconducting oxide films will attract much interest in the near future. Preliminary studies on the reaction of oxide superconductors with laser beams have already started (ref. 26).

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