

Thin Films of the **High- T_c** Bi-Sr-Ca-Cu Oxide System - A Brief Review

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(Received June 24, 1990)

The preparation, annealing conditions and substrate materials of the high- T_c oxide thin films are briefly surveyed. More in-depth discussion is devoted only to the Bi-Sr-Ca-Cu-oxide system.

I. INTRODUCTION

Since the initial¹ and subsequent^{2,4} discoveries of the high transition-temperature (T_c) superconducting mixed oxides, the research on this subject has been intensive and world-wide. Up to the present time, three oxide systems are known to yield reproducible results with T_c higher than **90**° K. They are: Rare earth-BaCu-oxide (RBCO): $T_c \cong 92$ K; Bi-Sr-Ca-Cu-oxide (BSCCO): $T_c \cong 110$ K; and Tl-Ba-Ca-Cu-oxide (TBCCO): $T_c = 125$ K.

The three systems are not dissimilar to one another. They share a number of common characteristics: (1) They contain Cu-oxide complex as an important ingredient which is deemed necessary for the occurrence of high- T_c superconductivity. (2) They are formed in highly anisotropic layer structures which consist of fundamental units of Perovskite type. (3) These structures are constructed with the framework of metallic ions and are stabilized by intricate oxygen bonds. (4) Their normal-state conductivity is hole-dominant and is due primarily to the subtle deviation from oxygen stoichiometry. (5) The valences of metallic ions are restricted to +2 and +3.

However, each system also maintains its individual traits. RBCO is most readily formed in single-phase and the undesirable impurities phase(s) can easily be distinguished and avoided. The crystal structure is comparatively simple and is rather easy to describe. The stability of the RBCO as a compound can sustain a wide range of oxygen variation (up to one oxygen atom per formula unit) although superconductivity is much less tolerant to such composition change. Moreover, nearly all rare-earth elements (except Sc, Pr, Tb and Ce) can form the high- T_c RBCO entity. Consequently, a wide variety of interesting research problems exist ranging from strong local magnetic moment for $R = \text{Gd}$ or Dy to no moment at all such as Y.

The BSCCO family consists of three known members which can be generally expressed as $\text{Bi}_x\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_x$ where $n = 1, 2, 3$. The three members, commonly designated as 2201, 2212 and 2223 according to the ratio of metallic ions, exhibit distinctly different T_c 's of 10-20, 70-80 and 105-115 K respectively.^{2,3} Under normal preparatory conditions, the 2212 type appears to be the most stable and is often the most dominant in presence even when the starting composition was aiming for 2223. The latter can be gradually stabilized with annealing just below the melting point. With 15% of Bi replaced by Pb, the 2223 type can be prepared in pure form. By T_c measurement alone, the individual member of the BSCCO family can be distinguished and studied separately. Therefore the BSCCO group provides the best opportunity to study the individual structure-related properties in the normal as well as superconducting states.

The TBCCO family resembles closely that of BSCCO. In addition to the 2201, 2212 and 2223 members, there also exist 1201, 1212, 1223 and possibly others. As far as achieving high- T_c is concerned, the TBCCO system is ideal. Since all members in this group exhibit superconducting transitions in the range of 80-120 K, multiphase samples of any combination always yield satisfactory results. This is probably why no effort has been reported to prepare single-phase material.

From the application point of view, depositing the high- T_c mixed oxides in thin-film form with desired superconducting characteristics is a first necessary step. Such effort has been already underway in many research laboratories and successful results have been reported in the literature. In this article, an attempt will be made to give an overview of thin films of only the BSCCO system.

II. HIGH- T_c OXIDE THIN FILMS IN GENERAL

II-1. Methods of preparation

There have been numerous articles reporting successful results in the deposition of high- T_c oxide thin films. The many approaches employed can be classified into three categories:

(1) Pulse-laser evaporation or laser ablation.

Since its inception⁶ the method has been successfully demonstrated widely but mostly for the YBCO system. Mainly a high-power well-focussed laser was repeatedly fired at a YBCO target pellet. The scattered material including vapor and spattered particles was collected on a substrate. One drawback with this approach is that it is difficult and inefficient to apply this technique for large scale operation. Moreover, the surface topology of the film may also be not as smooth as desired.

(2) Sputtering

This approach is the most powerful and most versatile of the three. It can be operated in a combination of various modes such as dc or rf, magnetron, reactive or inert medium, single or multiple targets etc. This technique is well-established in the industries and therefore will not post any problem for scale-up operation. However, associated with the

versatility, there exist a host of interrelated experimental parameters which have to be optimized together to yield desired results.

(3) Evaporation of individual metallic elements

The evaporation of the metals can be carried out either sequentially or concomitantly. A heat treatment at elevated temperature is absolutely necessary to promote the homogenization and oxidation of the metals.

11-2. Requirement of Post-annealing

Using the laser ablation or the sputtering process, the films deposited at ambient temperature are always amorphous. To induce crystallization and to stimulate the formation of the desired superconducting phase with proper oxygenation, a heat treatment at an optimum temperature and an atmosphere containing oxygen is necessary. This heating procedure can be carried out either during or after the deposition. The in-situ process is the most desirable because it can achieve the same effect at much lower temperatures. But it requires very stringent control of the substrate temperature during the film deposition and this requirement is often not trivial to meet.

11-3. Choice of substrates

In the history of superconducting thin-film study, there has never been a case in which the choice of substrate material becomes such a prominent topic as it is presently with the high- T_c oxide systems. The main reason for such development lies not with the post-deposition annealing requirement but with the reactive nature of the mixed oxides at elevated temperatures. In the past, films of excellent quality of superconductors such as Nb, NbN and Nb₃Sn have been deposited on Si and sapphire. Even common glass was demonstrated to be good substrate for Pb films. However for high- T_c oxide films deposited on practical substrates such as GaAs, Si and sapphire, the interaction and interdiffusion between film and substrate was so extensive that the desired superconducting phase was either poisoned or totally destroyed. It is now well established that the best substrate for high- T_c oxide films in all cases is SrTiO₃, a nearly-ferroelectric material. For those who are interested in microwave applications, SrTiO₃ was completely unacceptable because of its dielectric properties. A number of other materials have been tested and a list is given in Table I. Actually, MgO and LaAlO₃ have been demonstrated to be suitable substrate material⁷⁻¹⁰ in that both are relatively inert towards the high- T_c oxides and both exhibit reasonable dielectric behavior. The shortcoming is that both are uncommon. From the point of view concerning microelectronic applications, the realistic choices of substrate are none other than the practical electronic material GaAs, Si (quartz) and sapphire which so far have yielded very poor results in high- T_c films. To reconcile such disparity, the current research is in the direction of developing suitable buffer layer between the high- T_c oxide film and the substrate.

TABLE I. Choice of Substrates for Microwave Applications

Substrate	Dielectric Constant		Loss Tangent at ~ 10 GHz		
			300 K	77 K	4.2 K
SrTiO ₃	200-300 at 300 K	~ 2000 enormous at 77 K at 4.2 K	3×10^{-1}	8×10^{-2}	you do not want to know
YSZ (ZrO ₂)		25 -28	2×10^{-3}	8×10^{-4}	8×10^{-6}
MgO		9.6	4×10^{-4}	4×10^{-6}	1×10^{-6}
LaGaO ₃		25 -27	4×10^{-3}	1×10^{-4}	3×10^{-6}
LaAlO ₃		16	6×10^{-4}	8×10^{-6}	5×10^{-6}
Al ₂ O ₃		8.5 \sim 10.5	3×10^{-4}	9×10^{-7}	4×10^{-9}
Si		11.6	4×10^{-3}	- -	- -
GaAs		13	- -	- -	2×10^{-4}

III. BSCCO THIN FILMS

Among the three known polytypoids of the BSCCO system, 2212 is the most stable and therefore is most readily to form. Since the three members of the BSCCO family exhibit distinctly different T_c values, T_c measurement alone is sufficient to assess the prominence of the individual type. The 2223 type can be completely stabilized by partially replacing Bi by Pb at stoichiometry and with carefully controlled post-annealing.^{11,12} For bulk samples as well as thin films, such preparatory conditions must be observed, otherwise the 2212 type is always dominant in presence.

A wide variety of techniques have been reported in the literature. Without proper Pb substitution for Bi, the end products consisted of mostly the 2212 type and the T_c values were mostly in the range of 70-85 K, as summarized in Table II.

The net effect of adding Pb to the BSCCO material is the lowering of melting point by 20 \sim 30 C. Correspondingly, the required post-annealing temperature is lower and the 2223 structure becomes easier to grow. So far, there has been no report on the in-situ growth of 2223, which indicates that prolonged annealing is necessary for the 2223 formation. As summarized in Table III, all successful attempts in depositing 2223 films employed almost unanimously the technique of sputtering.³⁴ Included in the table is the result employing LaGaO₃ as substrate for BSCCO films for the first time. Actually the depositions were conducted with the same equipment, using the same parameters and following the same annealing procedures as films on SrTiO₃, LaAlO₃ and MgO. But only 2212, not 2223, forms on LaGaO₃. Preliminary examinations indicate that minute amount of Ga³⁺ ions have diffused into the film during annealing which possibly prevents the formation of the 2223 structures. This observation is consistent with the morphology of BSCCO films deposited on sapphire. The diffusion of Al³⁺ ions into BSCCO films is rather extensive. Short time annealing resulted only in the growth of 2212; heat treatment of long duration

TABLE II. Summary of BSCCO Thin Films (without Pb)

Deposition Method	Substrate	Heat Treatment		Zero Resistance at Reference	
		Temperature (C)	Duration (hr)	(K)	
Magnetron Sputtering	MgO	5 60-600	during deposition	56	(13)
	SrTiO ₃	880	10	90	
	MgO	875	0.5	100	(14)
	MgO	865	5	100	(15)
	MgO	880	1	72	(16)
Ion Beam Sputtering	MgO	645	during deposition	56	(17)
	MgO	825	2	75	(18)
CVD	MgO	910	during deposition	78	(19)
	MgO	800-850	during deposition	75	(20)
	MgO	800-900	during deposition	84	(21)
E-Beam Evaporation	SrTiO ₃			80	
	SrTiO ₃	850		72	(22)
Laser Ablation	Sapphire	860	1	72	(23)
	Si with SrTiO ₃ buffer layer	875		75	(24)
Electrolytic	MgO coated with Ag	8.50	1	70	(25)

TABLE III. The Formation of the 2223 entity in the BSCCO System (with Pb addition)

Substrate	Heat Treatment		T _c (K)		Predominant Phase	Reference
	Temperature C	Duration	Onset	Zero Resistance		
Al ₂ O ₃ (1 $\bar{1}$ 02)	800	1 hr	85	30	2212	(7)
	865	5 min	75	55		
SrTiO ₃ (100)	830	1 hr	85	54	2212	
	840	40 hr	113	104	2223	
LaAlO ₃ (012)	843	40 hr	113	90	2223	
MgO(100)	840	40 hr	110	90	2223	
LaGaO ₃ (001)	840	48 hr	88	80	2212	(26)
MgO(100)	850	15 hr	120	107	2223	(27)
	840	5-10 hr	120	110	2223	(28)
	855	50 hr	110	90	2223	(29)
	865	16 hr	115	106	2223	(30.31)
	850	3 hr	122	115	2223	(32)
	850	1-15	120	106	2223	(33)

led to the destruction of all superconducting entities.

Concerning the BSCCO system in general, there exist a number of important questions to be answered. No doubt Pb-doping facilitates the formation of 2223 structure. It is also known that for any Pb-doped BSCCO sample, the Pb content decreases continuously during heat treatment due possibly to the volatility of PbO. The Pb-depletion is particularly serious for thin films²⁹⁻³² and Pb-enriched atmosphere is recommended during annealing in order to compensate for the loss.

The drastic effect of oxygen on the superconducting transition and structure stability of YBCO is well documented. But for the BSCCO system, very little is known in this aspect. Up to the present time only qualitative work has been attempted.³⁵⁻³⁷ Important quantitative questions remain:

- (1) What are the extent and optimal temperature range of oxygen absorption and desorption?
- (2) Is there any oxygen-related phase transformation?
- (3) Where are the exact locations of individual oxygen ions relative to metal ions in the structure?
- (4) What are the upper and lower limits of oxygen content beyond which the structure becomes unstable?

For high- T_c superconducting oxides at large and more emphatically for the BSCCO system, thin films are formed with the (001) direction of the structure (2212 or 2223) perpendicular to the plane of the substrate. This observation is often loosely termed "epitaxial growth" in the literature. However, since this phenomenon has occurred so often that it seems to be independent of the substrate material, as illustrated in Fig. 1 and 2 (It may well

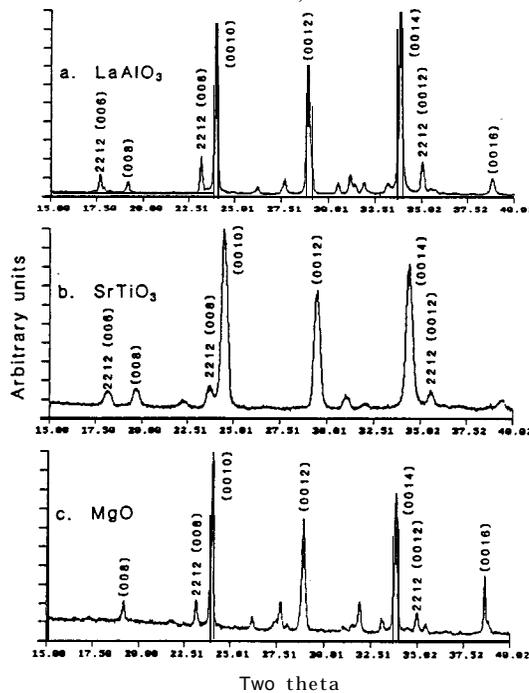


FIG. 1. X-ray diffraction patterns to illustrate the (001) preferred orientation of the 2223 structure in BSCCO films deposited on (a) LaAlO_3 ; (b) SrTiO_3 ; (c) MgO . The diffraction peaks corresponding to the substrates have been removed for clarity. The (001) peaks are individually identified. All minor peaks correspond to other planes of 22 12/2223 phases.

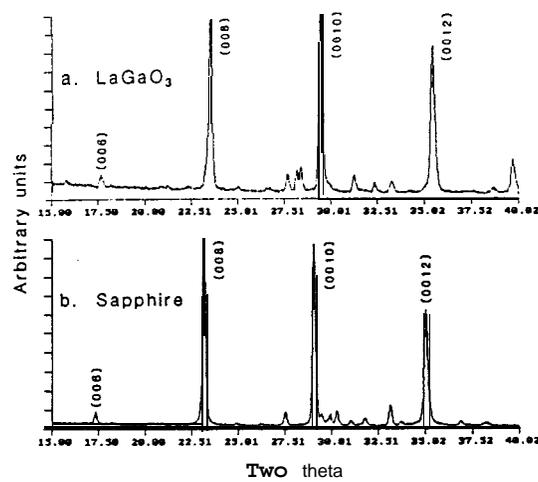


FIG. 2. X-ray diffraction patterns, illustrating the (001) preferred orientation of BSCCO 2212 films on (a) LaGaO₃; (b) Sapphire. The diffraction peaks corresponding to the substrates have been removed for clarity. The (001) peaks are individually identified. Nearly all minor peaks correspond to other planes of 2212 phase.

depend on the annealing procedures.) Between the 2212/2223 films and the various substrates tested, there must have existed gross lattice mismatch which is essential for epitaxy. Therefore a more appropriate term ought to be "preferred orientation". Such a description simply states that the layer structures of 2212/2223 favor to align the layer parallel to the substrate plane.

There is a strong benefit associated with the occurrence of preferred orientation. It is known that superconduction of the high- T_c oxides occurs mostly along the a-b plane (along the layers). When all the grains align in the a-b plane, the critical current density (J_c) is then greatly enhanced. The observed preferred orientation simply means that the J_c -value along the plane of substrate is high. Happily this is exactly the configuration necessary for all potential applications.

At the moment, the data on transport measurement of J_c on BSCCO films is rather rare. The next best thing is to estimate the J_c value through magnetization (M) experiments. Displayed in Fig. 3 are hysteresis curves of a typical 2223 film at various temperatures. At a first glance, the absolute values of M at field (H) larger than 1.5 T appears to be unusual because they increase with increasing H . This observation can be attributed to the diamagnetic contribution of the SrTiO₃ substrate as shown in Fig. 4, which yields a susceptibility value of 5.04×10^{-7} emu/Oe-cm². After correction for substrate and using the model of large flat plate^{38,39} J_c is calculated, as shown in Fig. 5.

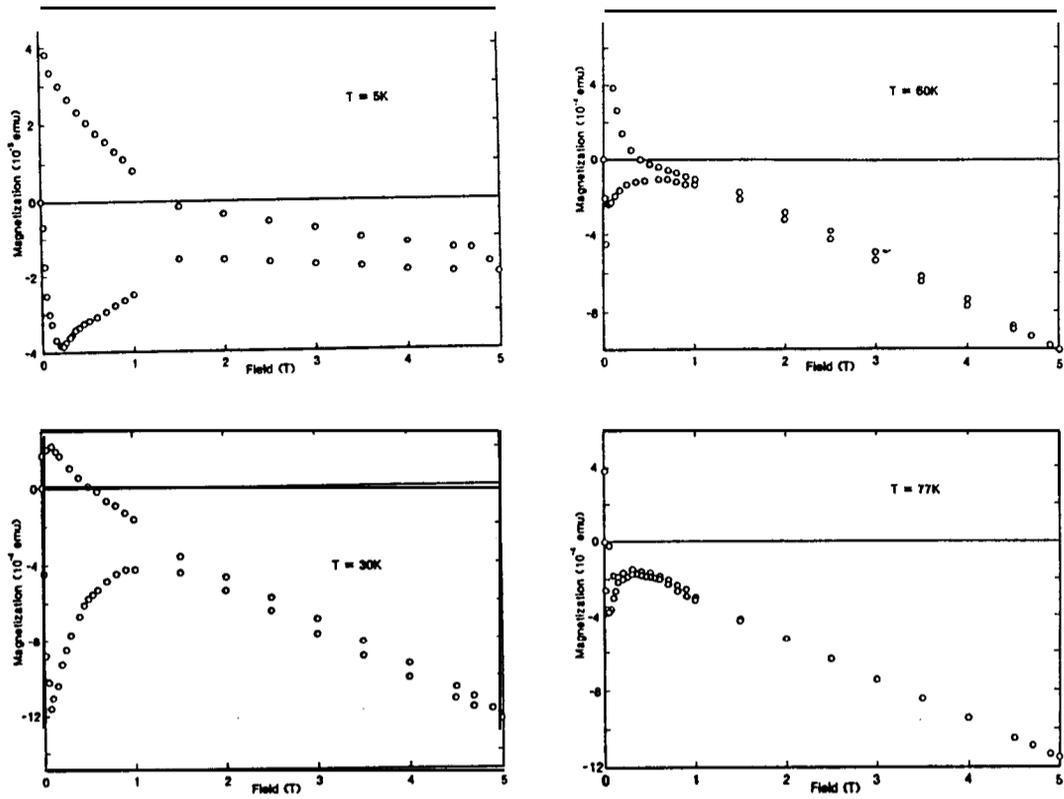


FIG. 3. Hysteresis plots of a typical BSCCO film (on SrTiO₃) at (a) 5 K, (b) 30 K, (c) 60 K, and (d) 77 K.

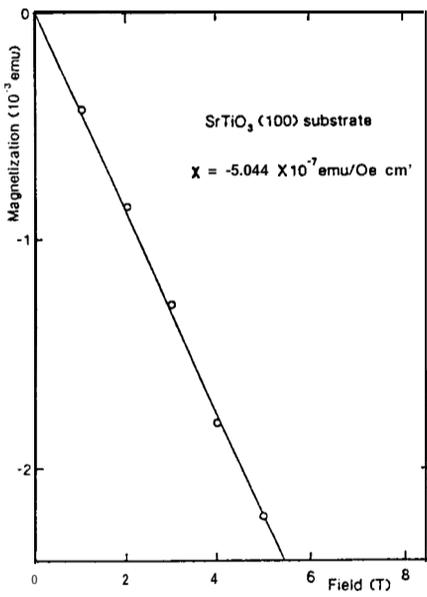


FIG. 4. Magnetization of a blank SrTiO₃ substrate to show its diamagnetic behavior.

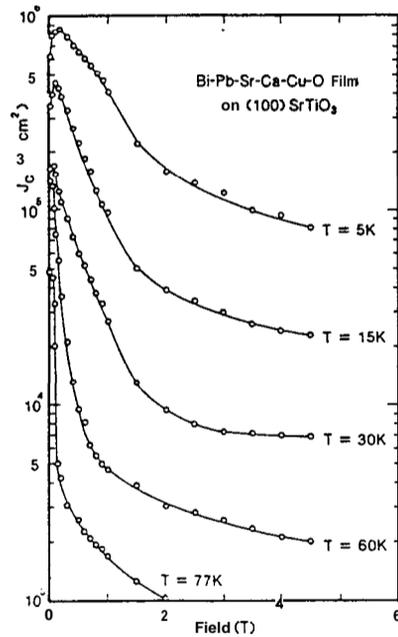


FIG. 5. Critical current density of a 2223 film, calculated from magnetization data using the flat-plate model.

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