

Invited Rev. Presented at 4th Int. Conf. Surf. Modif. Technol., Paris, 1990
Surf. Modif. Technol., in press, 1991

HC 1.5-9 1990
Conf 901108 1

A REVIEW OF BASIC PHENOMENA AND TECHNIQUES FOR SPUTTER-DEPOSITION OF HIGH TEMPERATURE SUPERCONDUCTING FILMS

O. Auciello,^{1,2} M. S. Ameen,² A. R. Krauss,³
A. I. Kingon,² and D. J. Lichtenwalner²

CONF-9011108--1

DE91 006468

1. Microelectronics Center of North Carolina, Research Triangle Park, NC 27709-2889
2. North Carolina State University, Materials Science and Engineering, Raleigh, NC 27695-7919
3. Argonne National Laboratory, Chemistry Division, Argonne, IL 60439

ABSTRACT

The processes involved in plasma and ion beam sputter-deposition of high temperature superconducting thin films are critically reviewed. Recent advances in the development of these techniques are discussed in relation to basic physical phenomena, specific to each technique, which must be understood before high quality films can be produced. Control of film composition is a major issue in sputter-deposition of multicomponent materials. Low temperature processing of films is a common goal for each technique, particularly in relation to integrating high temperature superconducting films with the current microelectronics technology. It has been understood for some time that for $Y_1Ba_2Cu_3O_7$ deposition, the most intensely studied high- T_c compound, incorporation of sufficient oxygen into the film during deposition is necessary to produce as-deposited superconducting films at relatively low substrate temperatures. Recent results have shown that with the use of suitable buffer layers, high quality $Y_1Ba_2Cu_3O_7$ sputtered films can be obtained on Si substrates without the need for post-deposition anneal processing.

This review is mainly focussed on issues related to sputter-deposition of $Y_1Ba_2Cu_3O_7$ thin films, although representative results concerning the bismuth and thallium based compounds are included. A complete review covering every aspect of all the high- T_c compounds would be far too lengthy.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

INTRODUCTION

The discovery of the new high temperature superconducting materials (1-4) initiated an intensive research effort in a wide variety of processing techniques in order to produce these new materials in different forms, which would allow utilization of the unique properties they possess. These materials were first synthesized in bulk form, probably because the hardware involved in producing them is less sophisticated than that necessary for thin film processing. However, thin films which are well oriented with respect to the substrate (usually c-axis up) possess higher current carrying capabilities than their polycrystalline bulk counterparts; this, and the potential for high T_c superconducting film integration into the microelectronics technology, indicates that perhaps the first practical applications of the new superconducting oxides will be in thin film form.

Presently, the high temperature superconducting compounds which appear to be the most promising, and have been studied most intensively in thin film form, are: 1) $Y_1Ba_2Cu_3O_{7-x}$ ($T_c \sim 93$ K), with other rare-earth elements sometimes substituted for Y; 2) $Bi_2Sr_2Ca_1Cu_2O_8$ ($T_c \sim 85$ K) and $Bi_2Sr_2Ca_2Cu_3O_{10}$ ($T_c \sim 110$ K), in which partial Pb substitution for Bi appears to enhance the growth of the 110 K phase; and 3) $Tl_2Ba_2Ca_1Cu_2O_8$ ($T_c \sim 97$ K) and $Tl_2Ba_2Ca_2Cu_3O_{10}$ ($T_c \sim 125$ K). Both the bismuth and thallium based compounds have a variety of related superconducting phases, which differ mainly in the number of Cu-O planes per unit cell. Although the high T_c of the thallium based compounds make them desirable for technological applications, the toxicity of thallium has delayed full scale efforts to study these compounds. At this time, it is not clear which materials will be most useful for any given application, because the superconducting properties and chemical compatibility with different materials differ.

The development of automated systems for the production of superconducting films in an integrated deposition/processing cycle will help meet the requirements for large scale manufacturing of these materials. Numerous techniques specifically developed for thin film deposition, and others adapted from more general coating technologies, have been applied for synthesizing high temperature superconducting films (5). It appears that techniques based on sputtering, laser ablation, or evaporation are emerging as deposition methods which are compatible with currently used techniques for device fabrication. These methods appear capable of producing the high quality, high purity, epitaxial films necessary to optimize device performance. Other techniques have been applied for the production of high T_c superconducting films, including, for example, chemical vapor deposition and spin-on processes. These methods, however, have not been studied as thoroughly as the physical vapor deposition techniques, and may not be as compatible than those mentioned above for the requirements of superconducting device fabrication technology. For example, spin-on processing of $Y_1Ba_2Cu_3O_7$ (6) produces films with poor grain-grain contact, and films must be subjected to an annealing step at > 900 °C in order to sinter the disconnected islands of superconducting material. Additionally, this method involves spin-coating of liquid solutions of suitable precursors onto substrates, or exposing them to jets of solution. In both cases the film deposition is generally followed by a lengthy drying process and sintering, which leads to extra (undesirable) steps in a manufacturing cycle. The microstructures and current density (J_c) values achieved with these techniques have not been as good as those obtained with vacuum deposition methods, but this may be due partly to the fact that not as much effort has been devoted to these techniques.

A manufacturing process for producing high temperature superconducting films for technological applications should at least include the following characteristics: 1) applicability of the processes to deposition of materials with different physical and chemical properties, 2) compatibility with integrated device processing, which includes production of as-deposited high temperature superconducting films on substrates at the lowest possible temperature, 3) production of high quality, epitaxial films with high critical currents, 4) simple and low cost deposition with capacity for high deposition

rates, 5) ability to produce patterned structures, superlattices and layered heterostructures, and 6) reproducibility of the deposition process.

In this review, only plasma and ion beam sputter-deposition techniques are reviewed, while a comprehensive analysis of vapor and laser ablation-deposition techniques can be found elsewhere (7). Additionally, this review will be limited to analyzing current technological developments in each method and basic phenomena related to the deposition processes. A thorough examination of these techniques, from the literature and our own work, has revealed a series of advantages and disadvantages for each method. The $Y_1Ba_2Cu_3O_{7-x}$ family of high T_c compounds (other rare earth elements can be substituted for yttrium) have been studied more fully than those of the bismuth or thallium based compounds. Therefore, this review focuses on the properties and preparation of sputter deposited $Y_1Ba_2Cu_3O_7$, and presents only a limited discussion concerning the preparation and properties of the Bi-Sr-Ca-Cu-O and Tl-Ba-Ca-Cu-O classes of high temperature superconductors. It is impossible to cite all the literature in this rapidly growing field of research; therefore, only representative references will be cited.

REVIEW OF DEPOSITION/PROCESSING TECHNIQUES

Plasma Sputter-Deposition

Systems and Phenomena

In plasma processing techniques (5), deposition of high temperature superconducting films is achieved by sputtering targets exposed to a dc or rf plasma discharge generated in a high vacuum chamber back-filled with an inert gas to a pressure of 0.5-170 mTorr (dc or rf diode sputtering). Most studies have been performed in the 5-50 mTorr pressure range. For sputter deposition of $YBa_2Cu_3O_{7-x}$ films, pure Ar or mixtures of Ar and O_2 gases have been used to produce the plasmas, with the pure Ar plasmas yielding films with stoichiometries closer to that of the target, whenever stoichiometric compound targets and nominally unheated substrates were utilized (8-10). Presently, the most widely accepted reason for this plasma related effect on film composition is that films are bombarded by energetic neutralized oxygen ions during growth (as will be discussed later), resulting in a preferential sputtering of Ba and/or Cu from the growing films (11,12). This resputtering has also been seen to effect the composition of Bi-Sr-Ca-Cu-O films sputtered from a single compound target, producing significant variations in the Ca composition across the film (Shah (13)). It appears that deposition of the Tl based compounds also suffers from similar effects (Subramanyam et al. (14)).

In these plasma-based techniques, the sputtering plasma is adjacent to the solid target, composed of a single compound ($YBa_2Cu_3O_{7-x}$, for example), or elemental target materials (Y, Ba, Cu or their oxides, for example) symmetrically distributed in front of a substrate. Typical substrate to target separation distances range from ~2 to 10 cm. The target is negatively biased (cathode) so that its surface is bombarded by positive ions from the plasma. It is common practice to use magnetic fields to form electron traps which are configured such that the $E \times B$ electron drift currents converge on the cathode surface. This technique, termed magnetron sputtering (Fig. 1), results in a higher plasma density, and therefore higher cathode (target) erosion rates and lower discharge voltages than obtained using diode sputtering methods (15). Magnetron sputter-deposition is one of the plasma based techniques most widely used at the present time.

The plasma sputter-deposition techniques do have difficulties, especially when multicomponent oxides are used as targets, as is the case when producing high T_c superconducting thin films by using a bulk superconductor target. As explained, it is difficult to change and control film stoichiometry when using a multicomponent target,

particularly as the number of components increase. Preferential sputtering and ion bombardment-induced surface topography can be severe if precautions regarding the ion bombardment parameters are not taken; i.e. continuous rotation of the target during sputtering to smooth directional ion-induced surface roughness that would otherwise be produced when using static targets (16). Other problems, related to obtaining layered structures and tailoring the film composition, are discussed below.

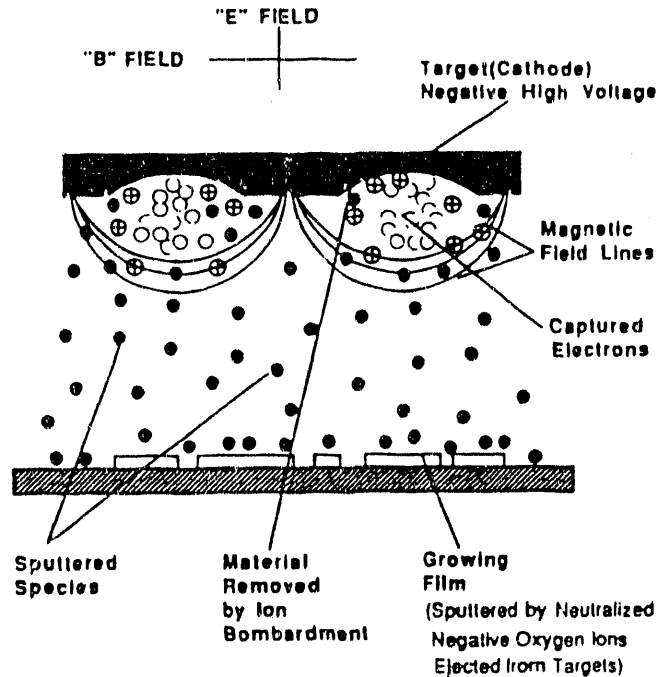


Fig.1. Cross-sectional view of a magnetron sputtering system for deposition of high T_c superconducting films.

Preferential sputtering results in compositional changes both in the lateral direction and to a certain depth below the surface of the sputtered target, in the normal direction. There are corresponding compositional changes in the sputtered flux, and therefore in the deposited films. This is a transient condition, since a steady-state situation is generally achieved in which the sputtering rate of the components of the material are proportional to the bulk composition (17). However, in many cases, a relatively thick layer must be removed before the steady-state condition is reached (17), which can require bombardment of the target for as long as 10 hours (18) before the deposition starts. This extended bombardment may in turn lead to the development of substantial surface topography (19), which can also affect the sputtered fluxes of the target materials.

To overcome the problems mentioned above, some groups (5), have used elemental materials (Y, Ba, Cu), or their oxides (Y_2O_3 , BaO_2 , and CuO , for example) in multitarget arrangements, where each material constitutes a cathode of a magnetron sputtering system. While this method addresses the issue of preferential sputtering, other problems are raised. Simultaneous sputter-deposition from elemental target materials exposed to independent magnetron sources leads to compositionally inhomogeneous films. Because the targets are located in different positions, the overlapping deposition fluxes will not be identical at all points on the substrate (20-22). This may present a problem in relation to coverage of large areas with films of uniform stoichiometry and thickness, which must be overcome for applications in the microelectronics technology,

where the industry is evolving into processing of single large wafers (≥ 5 inches). One method to improve compositional homogeneity with multiple sources is to increase the substrate to target distance, but this results in a very inefficient use of target materials. An alternative is to maintain a fixed substrate-target geometry by moving the substrate sequentially into position in front of each fixed source and alternately depositing thin layers of each material.

Recently, other problems related to plasma-assisted deposition have been identified, which are common to methods involving both bulk oxide superconductor targets or elemental or oxide multi-target arrangements. Impurity incorporation into plasma sputter-deposited films may occur frequently, due to the interaction of the plasma with the walls of the deposition chamber.

A major problem, as mentioned briefly above, is the bombardment of the growing films by energetic neutralized oxygen ions, causing resputtering of the depositing film. A relatively large number of O^- ions can be produced during the sputtering of oxide targets. These ions are accelerated through the plasma-cathode potential fall and neutralized upon entering the plasma region. The neutralized O atoms travel through the plasma and impact on the growing films with enough energy to produce undesirable damage and/or sputtering of the film. This phenomenon, designated as the "negative ion effect", has recently been demonstrated during magnetron sputter-deposition of Y-Ba-Cu-O films from a $YBa_2Cu_3O_{7-x}$ compound target (12) and a Y_2O_3 , Ba_2CO_3 , and CuO multitarget arrangement (11). Major consequences of the secondary particle bombardment of the growing films that have been observed are: (i) a dramatically reduced ion current to the target (reduced sputtering rate) and increased erosion of, and damage to, the growing film (Fig. 2a) with an associated stoichiometry change (Fig. 2b); (ii) in extreme cases, the negative ion effect can actually be severe enough to produce negative growth rates; (iii) in the case of the elemental-oxide target arrangement mentioned above, where the substrate is sequentially positioned under each target, film erosion has been observed only under the Y_2O_3 and Ba_2CO_3 but not under the CuO targets, which has fueled some speculations that not only neutralized O^- but also other energetic sputtered neutrals particular to each oxide may contribute to the film erosion (11); and (iv) another effect observed in the bulk superconductor target case is the rather strong variation in the deposition/erosion rate as a function of the radial position of the substrate under the target (Fig. 3). These large resputtering effects have also been clearly demonstrated to occur (Shah (13)) during the reactive magnetron sputtering of Bi-Sr-Ca-Cu-O films. As shown in Fig. 4, films deposited directly under the center of the target contain extremely high Ca concentrations, and the Ca content drops by a factor of four upon moving radially outward from the center, in a distance of only 3 cm. This compositional nonuniformity could be minimized by increasing the total system pressure, or by decreasing the oxygen partial pressure. Klein et al. (23) show that during rf sputtering of Y-Ba-Cu-O, the composition is a function of the chamber pressure, the applied rf power, and substrate position.

A number of different methods have been implemented in order to control the negative ion bombardment effect. A straightforward method is to increase the plasma pressure such that the energy of the neutralized negative ions is reduced, by multiple collisions with plasma species, until it is below the energy necessary to resputter the growing film (24). A second means of obtaining the appropriate film stoichiometry is to modify the target composition in order to compensate for the preferential sputtering associated with the negative ion effect (25). This method is time-consuming and somewhat unreliable since any change in processing parameters may alter the final film stoichiometry. However, this method has often been utilized. Unconventional sputtering geometries, in which the substrate is not subject to ion impact (termed "off-axis sputtering, Fig. 5 (26)), may ameliorate the negative ion effect, at the cost of film thickness uniformity and deposition rate. This latter factor can be reduced by as much as two orders of magnitude, which may represent an undesirable situation for commercial applications of this deposition technique.

In addition to the negative ion effect discussed above, bombardment of high T_c superconducting oxides by ions originating in the plasma results in a relatively high yield of secondary electrons, which also bombard the growing film. These electrons may also contribute to altering the film stoichiometry and characteristics, increase substrate temperature beyond that purposely and independently established for film processing, and possibly lead to electron bombardment-induced defects. Terada et al. (27) have recently investigated different methods (Fig. 6) for minimizing the bombardment of growing films by secondary electrons and ions emitted from the target, in an attempt to elucidate their contributions to undesirable changes in the film characteristics.

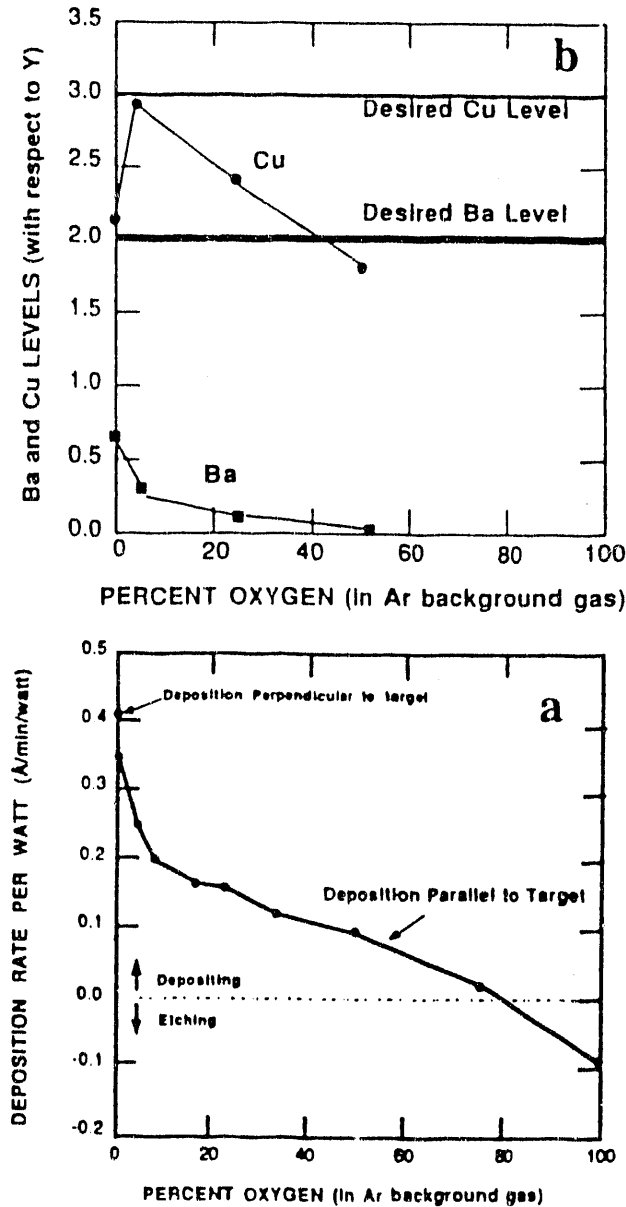


Fig. 2. (a) Net magnetron sputter-deposition rate for $YBa_2Cu_3O_{7-x}$ as a function of O_2 concentration in deposition chamber background gas. (b) Composition of a magnetron sputter-deposited Y-Ba-Cu-O film, normalized to Y=1.0, as determined by RBS (Rosnagel and Cuomo (12)).

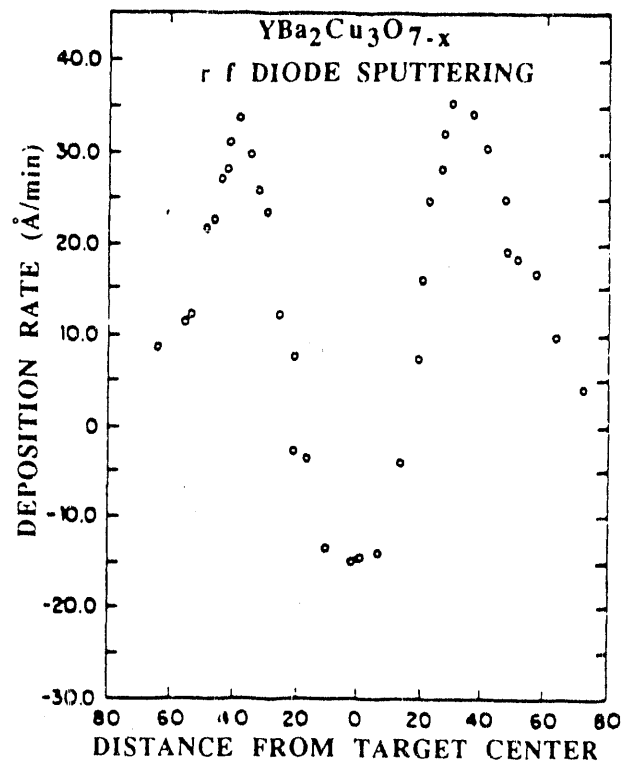


Fig. 3. Deposition/erosion rate as a function of the radial position of the substrate under the target (Shah and Carcia (11)).

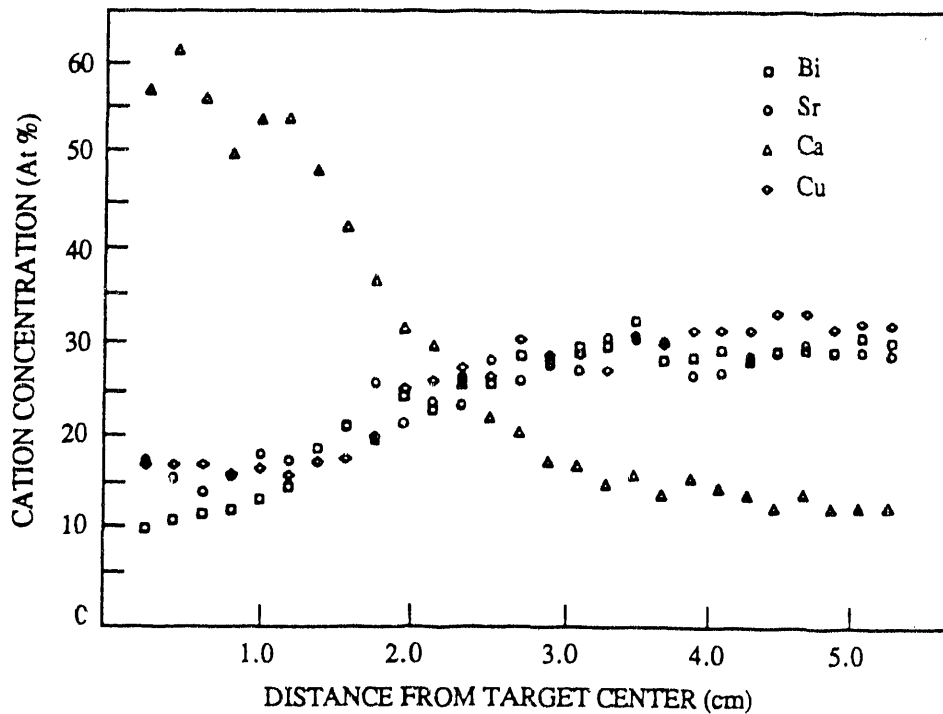


Fig. 4. Cation composition at different radial positions underneath the target. Films were deposited in 5 mTorr of Ar+10% O₂ sputtering gas with a target-substrate separation of 5 cm (Shah (13)).

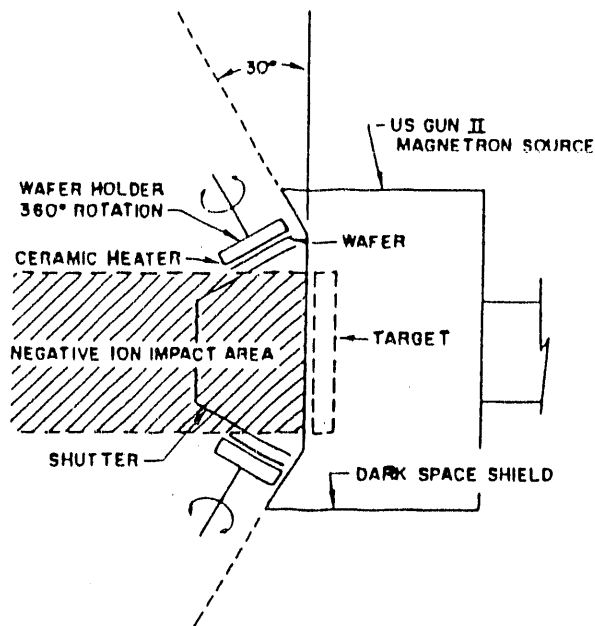


Fig. 5. Sketch of an unconventional geometrical arrangement of substrates out of the main stream of sputtered-neutralized negative ions to minimize the plasma-induced negative ion effect in plasma-assisted deposition of superconducting films (Sandstrom et al. (26)).

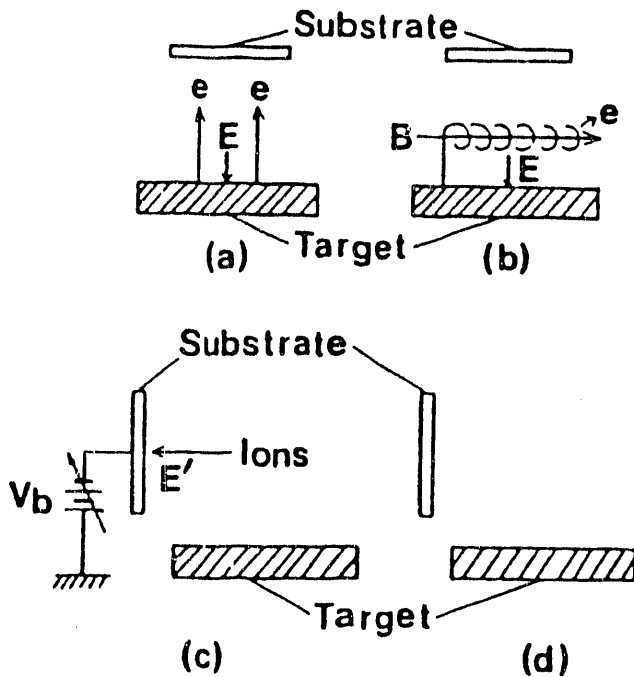


Fig 6. Methods for minimizing or eliminating secondary electron and ion bombardment of growing high T_c superconducting films in plasma sputter-deposition (Terada et al. (27)).

The experimental arrangements shown in Fig. 6 result in the following situations: (a) Both secondary neutralized ions and electrons impact the substrate. (b) Bombardment of secondary electrons is largely eliminated by trapping in a transverse magnetic field; although neutralized secondary ions can still impact on the substrate. (c) Bombardment of the substrate by secondary ions is controlled by bias voltage (it is not clear which secondary ions the authors are considering). (d) Bombardment of both secondary electrons and ions is eliminated. Again, it is not clear from the discussion presented by Terada et al. (27) what is the main difference between (c) and (d), although a negative bias in case (c) would induce ion bombardment from the plasma, which is different than the secondary (neutralized) ions being discussed.

The analysis of films deposited under conditions (a) and (b) yielded compositions as indicated in Table 1. Terada et al. (27) show that the suppression of electron bombardment in condition (b) resulted in films which are closer to the stoichiometric composition. Note that even without the electron bombardment (b), the negative ion effects still cause significant compositional changes when sputtering at low pressures.

Table 1. Relationship between film compositions and deposition conditions, from Terada et al. (27).

Press. mTorr	Composition Deposited	
	(a)	(b)
60	Y _{1.0} Ba _{0.68} Cu _{1.0}	Y _{1.0} Ba _{1.8} Cu _{3.0}
10	Y _{1.0} Ba _{0.30} Cu _{0.5}	Y _{1.0} Ba _{1.2} Cu _{0.8}

The gas pressure may also play a relevant role in slowing down these secondary electrons by collisions with plasma species (mainly ions and neutral atoms). Recent work performed by Auciello et al. (28) indicates that the intensity of the secondary electrons emitted from YBa₂Cu₃O_{7-x} targets exposed to Ar plasmas is significantly reduced as the gas pressure and distance from the target increase. The secondary electron spatial profiles observed suggest that the effects due to secondary electron bombardment of the growing film may be controlled by an appropriate positioning of the substrate (anode) with respect to the target (cathode) (28).

In any case, film compositional changes (with respect to the target composition) have been observed in both normal diode (where large number of energetic secondary electrons emitted from the target reach the substrate) and magnetron sputtering systems (where secondary electrons tend to be more effectively trapped close to the target (see Fig. 1)). This indicates that electron bombardment may not be a major contributor to film stoichiometry alteration, but that bombardment by energetic neutralized oxygen ions (or other sputtered negative ions) is a dominant phenomenon in both types of plasma-sputtering systems. If proper sputter-conditioning of the target is not performed, compositional differences may also be due to preferential sputtering of the target.

A commonly used method for correcting changes in film stoichiometry, caused by neutralized oxygen ion and energetic electron bombardment of the growing films, is to use compositionally adjusted targets, as discussed below.

Recently, Geerk et al. (29) have shown that a modified hollow cathode technique, which they named an "inverted cylindrical magnetron" (ICM) can be used to effectively eliminate the effects of both energetic ions and electrons during growth. This technique also provides both a higher deposition rate and better uniformity than the typical off-axis geometry often used. The essential features of the ICM geometry are shown in Fig. 7.

Note that the substrates are perpendicular to the target surface, eliminating energetic ion bombardment, and energetic electrons will be collected mainly by the anode. The deposition uniformity is also improved by the circular symmetry. This technique has been used to produce epitaxial films of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ with excellent superconducting properties (29). It appears that this sputtering geometry is the most effective yet applied for deposition using single compound targets.

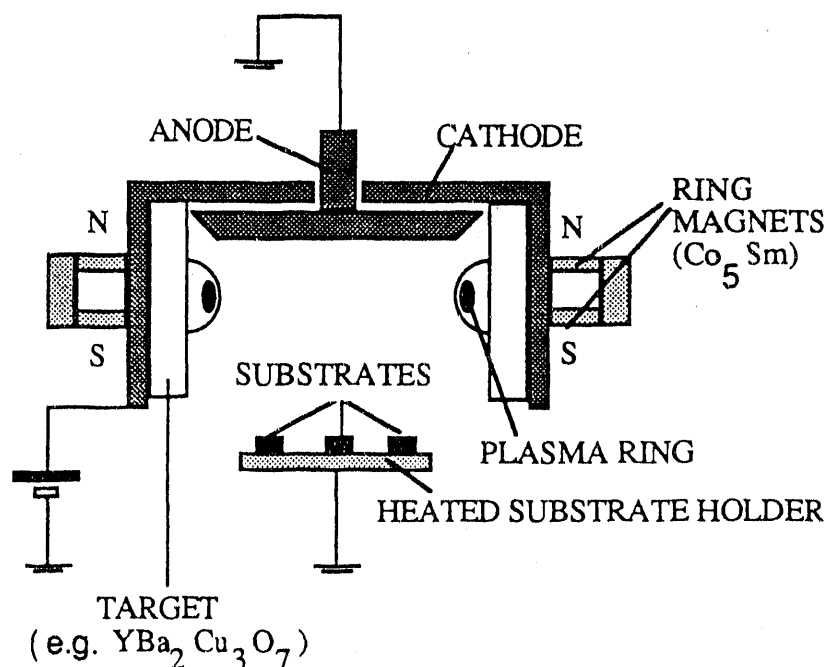


Fig. 7. Schematic cross-sectional view of the cathode, targets, magnets and substrates arrangement in the inverted cylindrical magnetron (ICM) sputtering system (Geerk et al. (29)).

Targets

Different targets have been used in plasma sputter-deposition of high T_c superconducting films. These can be classified into two main groups, namely: (a) sintered oxide and (b) metal or alloy targets. Initially, stoichiometric $\text{YBa}_2\text{Cu}_3\text{O}_7$ bulk superconductors were used as targets, but frequently resulted in deficiencies of Cu (24, 30-32) or Ba (9, 11, 12, 30, 33) due to resputtering of Cu and Ba from the growing films by the particle bombardment described in the previous section. Therefore, targets with excess Ba and/or Cu have been used to achieve the film stoichiometric corrections mentioned above. Specifically, Ba and/or Cu compensated targets with compositions (Y:Ba:Cu) such as 1:6:7 (31), 1:2:4.5 (24, 32, 34-36), 1:4.4:3 (33), 1:3.2:3.9 (30), 1:3.4:4.6 (37), 1:3:7 (38), 1:4:7 (39), 1:3:6 or 1:2.5:4.5 (40) have been used.

For deposition of the $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ compound, target compositions such as 2.2:2.2:2.2 have been used (Chen et al.(41)). In order to obtain the higher T_c $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}$ phase, the addition of Pb dopant is often used (partially substituting for Bi), and targets of compositions (Bi:Pb:Sr:Ca:Cu) such as 2:0.36:2.2:2.4:4.4 (Tseng et al.(42)), 2:0.3:1.6:2.5:3.6 (Lin et al.(43)), and 2.4:1.5:2.2:2.3 (Hakayura et al.(44)) have been successfully used. Films of the $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$ compound are generally sputtered from Tl-rich targets, with compositions such as 2.3:2:2:3 (Hong et al.(18)) and

2.4:2:2:3 (Subramanyam et al.(45)). Obviously, stoichiometric targets could be used if there were no sputter-induced compositional effects.

An alternative method for stoichiometry adjustment in the film involves the co-sputtering of both a stoichiometric target and a Ba or Cu target (for Y-Ba-Cu-O growth) simultaneously exposed to the plasma. Both metallic and oxide targets have been used in different experiments (31, 46, 47). Other groups have used either all three metallic targets for Y-Ba-Cu-O growth (48-51) and Bi-Sr-Ca-Cu-O growth (Face et al. (52)), or combinations of metallic and binary alloy targets, such as: Ba₂Cu₃ and Y (10, 50); YCu, BaCu, YCu₃, and Ba, sputtered in a 1:2 ratio (53); and Y, Cu, and Ba₂CuO₃ in a multitarget magnetron sputtering system (54).

In plasma sputter-depositions, in which metallic targets have been used, oxygen is generally added during film growing. This often has resulted in partially oxidized films. This partial oxidation is, however, not enough to prevent the material degradation upon exposure to atmosphere, which is particularly critical for YBa₂Cu₃O₇. Attempts have been made to minimize or eliminate this problem by deposition of a final overlayer of Y, followed by oxidation in a pure oxygen atmosphere (10), or by immediate post-deposition *in situ* or *ex situ* oxidation of the YBaCu metal films (10). A partial film passivation has been achieved by these methods. However, further work is necessary to significantly improve the films resistance to atmospheric-induced degradation.

The use of non-stoichiometric targets, and combinations of binary targets (two cations), to control film stoichiometry is highly empirical, and their potential to yield high quality films reproducibly is questionable.

Deposition Parameters

Parameters hitherto identified as relevant for plasma-assisted deposition of high T_c superconducting films include: (a) substrate temperature, (b) oxygen pressure (or activity), (c) gas pressure, (d) substrate-target distance, (e) target geometry, and (f) deposition rate.

Substrate temperatures used span the range from room temperature to 900 °C. Two general approaches have been used to deposit high-T_c films (Geerk et al.(29)). 1) Deposition at < 500 °C, which generally produces amorphous film as-deposited, and require post-annealing in an oxygen ambient at temperatures in the range of 850-950 °C to obtain the proper phase and oxygen content. The high temperature anneal results in films having very rough surfaces, and provides the opportunity for deleterious film-substrate interactions. 2) Deposition at higher temperatures, typically about 650-800 °C, which produces as-deposited superconducting films as long as sufficient oxygenation is provided during growth, followed by lower temperature oxygen annealing (24, 36). This technique produces very high quality films having extremely smooth surfaces. The use of higher substrate temperatures yielded non-superconducting phases. On the other hand, some groups have reported that as-deposited films with the crystalline orthorhombic phase were obtained at substrate temperatures as low as 400 °C (55) or 560 °C (56). However, neither the accuracy of the temperature measurements nor the exact plasma conditions under which those films were produced have been clearly established. Both Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O films of high quality have been produced as-deposited, although we are not aware of any reports of as-deposited films of the thallium based compound, presumably due to difficulties related to the high vapor pressure of Tl.

Presently, it is not known what is the lowest temperature that can be used to obtain as-deposited superconducting films. However, Bormann and Nolting (57) have shown that under equilibrium conditions, the oxygen pressure required to avoid decomposition of the Y-Ba-Cu-O perovskite structure increases with increasing substrate temperature. Hammond and Bormann (58) have shown that for *in situ* YBa₂Cu₃O_{7-x} growth, this stability criteria appears to be satisfied, indicating that a direct correlation

exists between substrate temperature and the oxygen pressure necessary to form the superconducting phase. Because the necessary oxygen pressures appear to be rather high, numerous attempts are being made to enhance the oxygen activity for film oxygenation by exposing them to energetic oxygen ions, generated by ion beams or plasmas, or to sub-eV atomic oxygen or ozone (O₃) jets (these issues will be discussed more fully in the section on film processing). From an analysis of various experiments presented in the literature related to *in situ* deposition of YBa₂Cu₃O_{7-x} films, it appears that three basic conditions should be satisfied to produce as-deposited superconducting films, namely: (a) the deposition should be done with the substrate at a temperature in the range 450-800 °C, (b) crystallization of the films during deposition must be complete, and (c) oxidation of the films during deposition and/or cooling down period must be sufficient to yield the correct crystalline phase and oxygen stoichiometry. As already mentioned, the sputtering parameters must obviously be properly adjusted in order to obtain the proper cation compositions.

The Y:Ba:Cu ratio needed to achieve a superconducting transition is not necessarily 1:2:3 (due to various possible cation site-substitutions, for example), but the closer to that ideal ratio the higher the T_c and the sharper the transition. Earlier Y-Ba-Cu-O films, for instance, that were deficient in Ba and Cu (e.g. 1:1.5:2.5) presented R vs. T curves very similar to the 1:2:3 material (30). This was explained by considering that the non-stoichiometric material still had the superconducting orthorhombic structure after an appropriate annealing (30). However, other researchers (59) observed that Ba and Cu deficient films resulted in a semiconducting behavior, above T_c, while Ba rich films generally resulted in R vs. T curves characteristic of a metal without a superconducting transition. In addition, it has been observed that the c-lattice parameter can vary in Y-Ba-Cu-O films (60, 61). This corresponds to a region of cation solid solution, viz incorporation of additional Cu-O planes, and is unlike the behavior of sintered ceramic YBa₂Cu₃O_{7-x} specimens. The observation of additional sets of Cu-O planes within the crystal structures of phases of the bismuth and thallium systems abounds, because of the many phases possible which have similar a-axis lengths but differ only in c-axis length (Liang et al.(62)). Therefore, off-composition samples may still appear to be single phase compounds, although they are often multiple phases which are atomically layered. Obviously, further work is warranted to clarify the interdependence of composition vs. crystallographic structure that result in superconducting films.

The target-substrate geometry is an issue which has received much attention in the quest for achieving *in situ* deposition at moderate substrate temperatures. Considerable spatial inhomogeneity has been observed in the sputtering flux of a plasma environment. This results in compositional variations across the film surface, as previously shown in Figs. 3 and 4. This effect is particularly pronounced in plasma systems involving a parallel plate geometry. It has been found, for example, that the center of an Y-Ba-Cu-O film was Y rich, while the fringes contained an excess of Ba. This could be due to either one or the sum of the "negative ion effects" and different collisional processes, in the plasma, for sputtered species with different masses, which can affect the sputtered flux distribution for different species. These effects may be important according to preliminary studies recently conducted by Auciello et al. (28). Both thickness profile and concentration variations of deposited films radially symmetric with respect to the target center location have been observed (46, 62).

Differences in the angular distribution of sputtered constituents in multicomponent materials may be a problem with planar targets (63), particularly for high ion bombardment doses that produce strong topographical changes on the target surface (19), which partially contribute to these variations through geometric effects (30). Wehner et al. (63) suggested a unique method for reducing the geometric effects introduced by the planar target geometry. They used a spherical target exposed to a Hg plasma (Fig. 8). Advantages that Wehner et al. (63) claim are particular of this system include: (a) the spherical geometry, which yields a more uniform sputter-flux angular distribution for all components of a multi-element target; (b) the use of a gas having a relatively low

ionization potential, such as Hg, which allows formation of a plasma with a low voltage, reducing the acceleration of the negative particles emitted from the oxide targets (O^- ions and secondary electrons, as discussed above), and therefore reducing the "negative ion effect". Disadvantages to be considered include: (a) the complexities in fabricating a spherical target, and (b) the use of a Hg plasma. The inverted cylindrical magnetron sputter-deposition concept described by Geerk et al.(29) appears to be a more practical approach to overcoming the various deficiencies of planar, single target sputtering.

The deposition rate may also affect the quality of the resulting films. Akune and Sakamoto (64) observed, for example, sharp superconducting transitions in Y-Ba-Cu-O films deposited at low rates, while others deposited at higher rates showed broad transitions. However, Wu et al.(65) have recently produced laser deposited Y-Ba-Cu-O films having excellent quality even at deposition rates as high as 14.5 nm/s. Therefore, it is probable that increased deposition rates are possible for sputter deposited films, although parameters affecting film composition may need readjustment.

In spite of the relatively large amount of information accumulated on plasma sputter-deposition of high T_c superconducting films, further work is necessary to better understand the phenomena involved and control the deposition parameters for optimization of film characteristics, and to establish the basis for a more reliable comparison with other techniques.

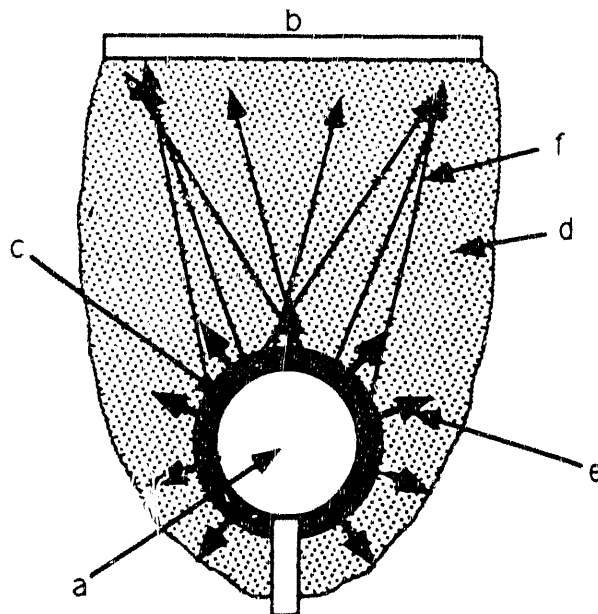


Fig. 8. Sketch showing a plasma sputter-deposition system with spherical target/planar substrate geometry. The radius of the sphere is 5 mm and the target-substrate distance 15 mm for this particular system. (a) is the spherical target, (b) is the substrate, (c) is the plasma sheath, (d) is the Hg plasma, (e) represents the negative oxygen ions, and (f) are the sputtered species (Wehner et al. (63)).

Ion Beam Sputter-Deposition

Ion beam sputter-deposition of high T_c superconducting films has been investigated much less than the methods previously discussed. However, this method is well suited for deposition of multi-component oxide films such as the high T_c oxide superconductors, since many of the undesirable effects (substrate bombardment by energetic negative ions and electrons, impurity introduction in films from plasma-wall interaction in the deposition chamber, etc.) already discussed for plasma sputter-deposition are not present or are much smaller in the ion beam sputter-deposition case. However, initial work using this technique involved the utilization of ion beams under rather uncontrollable conditions to sputter $YBa_2Cu_3O_{7-x}$ bulk superconductor targets. Improper confinement of the beams led to the introduction of impurities, which resulted in films with low T_c and poor characteristics (66). More recently, other researchers have used the ion beam sputter-deposition technique to produce high quality films from sputtering of superconductor targets (67), including the production of as-deposited superconducting Y-Ba-Cu-O films (23). Again, as in the plasma sputter-deposition method previously described, a rather long pre-deposition sputtering of the multicomponent targets was necessary in order to stabilize the target surface composition.

More recently, an automated ion beam sputter-deposition technique has been developed (68-71), which has the following features:

- (1) High current ion beams generated by either a Kaufman-type (72) or a capillaritron (73) ion source, which are directed at either 45° or near normal incidence with respect to the target surface normal (see Fig. 9). Fundamental studies on ion-solid interactions have revealed that the optimum geometry depends on the bombarding ions mass and kinetic energy, and the mass of the sputtered atom being deposited onto the substrate (74).
- (2) A rotatable target holder driven by a computer-controlled stepper motor, which serves to sequentially position elemental material (or their single oxide) targets in front of the sputter-beam (Fig. 9).
- (3) A QCR (Fig. 9), which measures the amount of each elemental material deposited and sends a feedback signal to the computer when the pre-programmed necessary amount of an element, to produce a desired film composition, is reached. The QCR feedback signal activates the computer for shutting off the ion beam while rotating the target holder to position the next target under the beam.
- (4) Various computer-operated controls to regulate: (a) the introduction of processing gases (oxygen for example) into the target chamber or in a sub-eV atomic or energetic ion beam source directed at the substrate, (b) the interposition of shutters or masks between targets and substrates, (c) the substrate temperature, including rump-up and down cycles, and (d) other processing steps.

A specially designed computer program (69) is a fundamental component of the automated ion beam sputter-deposition system. The potential of this technique has recently been demonstrated by producing superconducting $YBa_2Cu_3O_{7-x}$ films (71). To date, the highest T_c obtained with the automated ion beam sputter-deposition technique, for as-deposited films, is 88 K as measured by the Meissner effect (70, 75). However, much work is still needed to optimize the method. In particular, studies on basic ion beam-solid interaction phenomena, related to the elemental targets relevant to this review (Y, Ba, and Cu for example), are necessary. Comprehensive experimental and computer modelling studies, using the TRIM code (76), have recently been initiated in our laboratory, and first results have been published (74, 77). Briefly, these studies have shown that light ions such as Ar^+ impacting at 45° with respect to the target surface normal results in an undesirably high scattered ion flux, involving species with energies in the hundreds of eV range, when the ions impacting on the target have energies in the range of 1000-1400 eV. The flux of neutralized scattered ions from the target is directed at the substrate, which leads to a deleterious erosion of, and gas incorporation into, the film due to the impact of these species. It was found that by using Kr^+ or Xe^+ ions, the scattered ions effect can be minimized or eliminated (74, 77). Additionally, A mapping of

the sputtered flux angular distribution suggests that the QCR and the substrate should be positioned symmetrically with respect to the target surface normal in order to receive similar fluxes of sputtered species. Other results presently being analyzed will provide valuable information for the optimization of the system geometry.

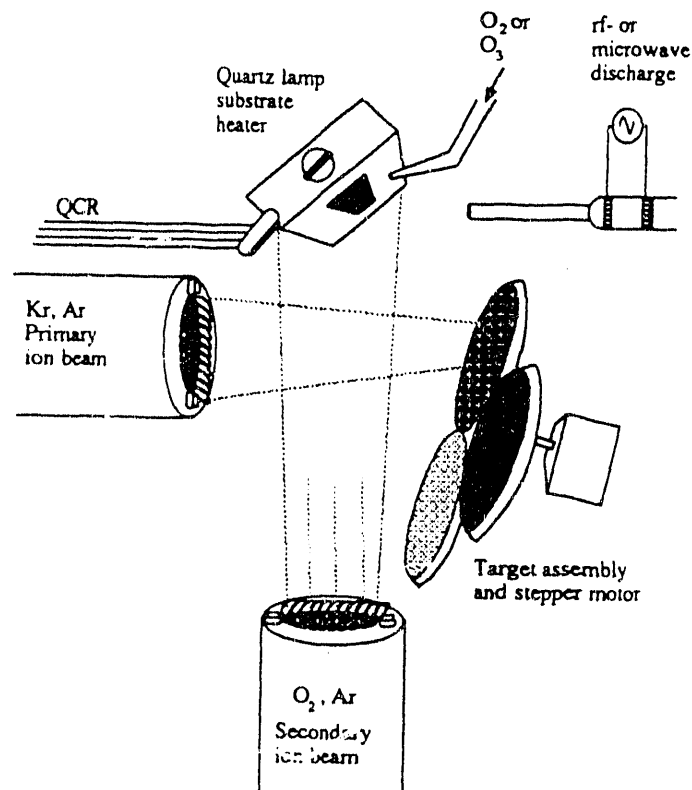


Fig. 9. Schematic of the automated ion beam sputter-deposition system. The computer monitors the quartz crystal resonator (QCR) output, turns the ion beam off, and rotates the targets when the desired amount of sputtered material is deposited (Krauss et al.(57) and Kingon et al. (58)).

Other groups are now developing ion beam sputter-deposition techniques involving the use of various beams to sputter elemental materials from different spatial locations and simultaneously deposit them onto an appropriately situated substrate. However, the automated ion beam sputter-deposition method described above has some advantages over those featuring multiple ion beams, namely:

(a) The use of only one ion beam, which simplifies hardware design and reduce cost, particularly when producing films with more than three components. This makes computer control more manageable and avoids having to accurately control various ion beam currents simultaneously.

(b) The sputtered fluxes of all elemental target materials originate from the same spatial location in the computer-controlled single ion beam system, which should contribute to the production of more uniform films across the substrate surface both in thickness and composition.

- (c) The ion scattering fluxes and angular distributions of the sputtered fluxes may be more easily controlled in the single ion beam system.
- (d) The geometry of the single ion beam system permits the installation of oxygen sources directed at the substrate, and focused beams for in-situ ion, electron, or laser beam-induced patterning.

Compared with the plasma sputter-deposition techniques, the ion beam method offers the following advantages:

- (a) A much lower partial pressure of impurities in the target chamber during deposition, since the focused beam can be made to mainly interact with the target, contrary to the plasma sputtering case, where the plasma has a rather strong interaction with the target chamber walls.
- (b) Controllability of the ion angle of incidence with respect to the target surface, and better control of the ion current and energy.
- (c) No negative ion bombardment of the growing film as in the plasma sputter-deposition case, which requires extra attention in relation to the target-substrate relative positioning.

FILM PROCESSING METHODS TO PRODUCE THE SUPERCONDUCTING STATE

Initially, a high temperature post-deposition annealing was required to produce the superconducting crystallographic structure in the deposited films. Subsequently, different methods were developed to synthesize as-deposited superconducting films. Both approaches are separately discussed in the following sections.

Method 1: Low Temperature Deposition, Post-Deposition Annealing and Oxygenation

Initial efforts to produce high- T_c thin films utilized low temperature deposition (< 500 °C), required a high temperature anneal to produce superconducting films. Deposition processes occurring at low temperatures and low oxygen activities result in amorphous, often oxygen-deficient, films. The high post-deposition anneal temperatures are necessary, since crystallization (into $YBa_2Cu_3O_{7-x}$, for example) requires both cation and anion diffusion. The oxygen stoichiometry of $x=0$ is achieved by a final anneal at an intermediate temperature, or by slowly cooling the film from the high temperature anneal, both processes being conducted in an oxygen atmosphere (78). The post-deposition heat treatments, for the case of Y-Ba-Cu-O films, were similar for all deposition methods. Differences in annealing procedures for forming the bismuth and thallium based compounds will be described separately.

$YBa_2Cu_3O_{7-x}$: Films are usually annealed at 850-950 °C for times running from a few minutes to several hours, depending on the film thickness and particular annealing conditions. Higher temperature annealing led to the formation of non-superconducting phases. Prolonged heating times appeared to increase the volume fraction of the perovskite phase in Y-Ba-Cu-O films, but simultaneously, new peaks appeared in the XRD spectra, which were attributed to either minor phase formation or film-substrate interaction (8).

An alternative annealing procedure used involved heating the films to lower temperatures (550-650 °C) for longer periods of time (about 20 h), in order to minimize substrate-film reactions (79). However, some researchers claim that the superconducting 123 phase of Y-Ba-Cu-O films does not crystallize below 700 °C, even for long annealing times (60 h), and temperatures ≥ 850 °C are necessary (80). The temperature needed for crystallization of the orthorhombic superconducting structure may depend on the crystallographic structure of the as-deposited films, with amorphous films needing higher temperatures than polycrystalline ones, as well as the amount of oxygen in the as-deposited film. Unfortunately, the crystallographic structure of the as-deposited films has

not been generally characterized before the annealing step. Therefore, it is presently difficult to make a critical analysis of the data available in the literature. If crystallization is achieved in as-deposited films at intermediate substrate temperatures (600 °C for example (81)), post-deposition annealing at relatively low temperatures (350 °C, as claimed by Hayasi et al. (81), for long periods of time, may also produce superconducting films. In fact, Hayasi et al. (81) claimed that a long annealing at 350 °C resulted in the formation of a so called orthorhombic structure I which yielded a higher T_c than a similar so called orthorhombic structure II produced at 550 °C.

Y-Ba-Cu-O films produced by sequential evaporation of Y, Ba, Cu layers, were obtained after annealing at temperatures in the range 650-950 °C for periods of time in the range 2 min-6 h, depending on the type of annealing (rapid thermal annealing (RTA) or slow oven treatment) (82-88). Some films deposited under strongly oxidizing conditions, on the other hand, became superconductors after annealing at relatively low temperatures (about 500 °C) (89-90).

The substrate material appears to have some influence on the annealing temperature necessary to produce an optimized superconducting structure. For example, Y-Ba-Cu-O films produced on SrTiO₃ presented the sharpest superconducting transition after annealing at 930 °C, but the highest T_c were obtained after heat treatments at 870-900 °C (82, 86, 91). Conversely, it appears that 920 °C is too high an annealing temperature to produce superconducting films deposited on ZrO₂ (92). Ma et al. (93), on the other hand, claimed that deposited layered structures such as Cu/BaO/Y₂O₃/Ag/SiO₂ were transformed into a superconducting film when annealed at 800 °C but not at 750 or 850 °C. Some researchers have suggested that a strategy to be followed would be to lower the annealing temperature as much as possible, within the thermodynamic conditions necessary to produce the appropriate crystallographic superconducting structure, and shorten the annealing time in order to minimize the film-substrate interface reaction, which has been demonstrated is deleterious to the superconducting characteristics of the films. It is not clear, from the published data discussed above, what the accuracy was with which the annealing temperatures have been measured. This should be clarified, considering that small differences in annealing temperatures appear to have marked effects on film characteristics.

In addition to the annealing temperature, the heating and cooling rates also appear to be important. High heating rates have been used by many groups. However, some experiments indicate that superconducting film characteristics may be improved by using slow heating rates during the annealing process (26). It is not clear yet what physical and/or chemical characteristics of the films are affected by the heating and cooling rates. However, some aspects that appear to be resolved for the annealing of Y-Ba-Cu-O films include:

- (a) for films < 1 μm thick, the rate of oxygen intercalation into the lattice is fast enough to go to completion even for fast cooling rates,
- (b) the twin structure, which has an effect on the superconducting characteristics of the films, is affected by the cooling rate, and
- (c) an effective oxidation is achieved by heating the films to 400-500 °C in an oxygen atmosphere at a pressure > 0.2 Torr.

Unfortunately, control of the annealing parameters, according to the published data, appears to have been largely based on empirical considerations, and it is not clear what influence numerous annealing cycle steps, introduced by different groups, have on the superconducting characteristics of the films.

Annealing times have also been varied within a wide range including a few minutes to hours. Relatively short times (1-5 minutes) and low temperatures have been used in annealing as-deposited multimetals (50, 53, 94). It is important to distinguish the annealing time and temperature for crystallization from the oxygenation time and temperature. RBS measurements have shown, for example, that oxidation of Y-Ba-Cu films were complete after 30 minutes at 250 °C, but the formation of the 123 perovskite

structure required heating the films above 500 °C (50). Other work has shown that the maximum oxygen uptake rate for Y-Ba-Cu films occurs at about 400 °C (33). However, work prior to 1988 has to be considered critically, as many experiments were not properly controlled.

Rapid thermal annealing (RTA) has been investigated by different groups as an alternative annealing procedure. Unfortunately, researchers have also implemented this method by relying on empirical bases. This may be a reason for some contradictory results. In one report, for example, Y-Ba-Cu-O films deposited on Si or SiO₂ substrates exhibited zero resistance at 40-66 K after RTA, which involved heating the films to 920 °C in 5 s, maintaining them at that temperature for 8 s, and finally cooling them to room temperature in 80 s (95). Ma et al. (93), on the other hand, were able to produce superconducting films on MgO, by using the RTA technique, but failed to do the same for films deposited on Si or SiO₂.

Bi-Sr-Ca-Cu-O: A typical annealing process for obtaining superconducting Bi₂Sr₂CaCu₂O₈ films involved heating at 865 °C for 20 min in O₂, followed by 850 °C for 5 hrs (Dhere (96)). Melting of the film occurs during the 865 °C step, which is effective in improving the film homogeneity. Superconducting films with partial Pb substitutions for Bi have been obtained by annealing at just below the melting temperature (Guarnieri et al.(97)), and it has been suggested that the Pb partial substitution helps to form the Bi₂Sr₂Ca₂Cu₃O₁₀ phase. Although the Pb may evaporate during the anneal, the higher T_c obtained remains intact (Osborne et al.(98)).

The optimum annealing conditions depend on the film composition, as well as on a complex interrelation between annealing time and oxygen pressure. Face et al.(52) have shown that lower temperature anneals require lower oxygen pressures to be successful. In fact, the melting temperature of the film appears to be a function of the oxygen pressure (Dhere (96)). Clearly, if this material is to be used in any multi-layered devices, melting would have to be avoided.

Tl-Ba-Ca-Cu-O: The annealing process for the thallium based compounds serves not only the purpose of producing crystallinity and the proper O content, but must also serve to bring the Tl concentration to stoichiometry. To date, all films of the various Tl compounds have required post-deposition anneals in order to produce the superconducting phase. Typically, films are annealed in a sealed container [such as an alumina crucible (Subramanyam et al.(14) and Cooke et al.(99)) or quartz tube (Hong et al.(18))] along with pressed pellets of the Tl-Ba-Ca-Cu-O composition desired, in an air or oxygen environment. The sealed container keeps the Tl containing vapors from escaping, and the bulk pellets serve to keep the Tl partial pressure at the equilibrium value for that compound. Annealing temperatures vary from 750 to 880 °C, and times from 5 to 30 minutes appear to be sufficient (Hong et al.(18), Cooke et al.(99), and Subramanyam et al.(14)).

Method 2: In Situ Deposition without Post-Processing

The high temperature post-deposition anneal can result in deleterious substrate-film interactions, making this particular process incompatible with the Si-based semiconductor technology. Therefore, much work has been directed during the past two years at modifying the techniques discussed above to produce as-deposited crystalline superconducting films at substrate temperatures ≤ 600 °C (25, 89, 100-106). Production of films at substrate temperatures ≤ 600 °C is critical for the application of high T_c superconducting films to device technologies, particularly the Si-based semiconductor technology. Presently, much success has been achieved in the production of as-deposited films of both Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O. Thallium based materials have not been superconducting as-deposited to date, presumably due to difficulties related to the high

vapor pressure of thallium. The *in situ* deposition of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ has been investigated most intensively to date, and is the main focus of the following discussion.

For the deposition of *in situ* Y-Ba-Cu-O, it appears that the most critical factors are the control of substrate temperature and oxygen pressure. Bormann and Nolting (57) have determined the conditions of temperature and pressure under which the perovskite phase is thermodynamically stable (with respect to decomposition into other oxides). Somewhat surprisingly, it has been shown by Hammond and Bormann (58) that films produced *in situ*, by a variety of researchers, fall within this stability region. Therefore, although thin film deposition is a very non-equilibrium process by nature, the aspects of oxygen incorporation and phase stability appear to be governed by thermodynamic criteria at these higher deposition temperatures. From this equilibrium criteria, films deposited at 700 °C require an oxygen partial pressure greater than 20 mTorr in order to obtain the (tetragonal) perovskite structure (increasing the O_2 pressure during cooling is sufficient for obtaining the orthorhombic, superconducting, phase). Because some types of vacuum processes can not operate at these high required pressures, researchers are investigating the use of more active forms of oxygen species. Because the oxygen activity, or chemical potential, is the real factor to be considered, lower fluxes of more active species should be adequate.

Different methods, depending on the deposition technique used, have been utilized to dynamically introduce oxygen into the growing film in order to produce as deposited high T_c superconducting films at the lowest possible substrate temperature. Some examples are the use of active oxygen from plasma discharges or the use of ozone (107). Although not directly related to this paper, it is relevant to discuss the film oxygenation methods developed for the laser ablation-deposition technique because of the insight that can be gained in relation to applying similar approaches for sputter-deposition techniques. Witanachchi et al. (101), for example, first demonstrated the use of an oxygenated laser-induced plasma-assisted deposition method for producing as deposited Y-Ba-Cu-O superconducting films at about 400 °C. They located a positively biased (about 300-400 eV) platinum ring in front of a grounded target, which was used to sustain an oxygenated plasma triggered by the laser-induced plasma plume from the target, in combination with an oxygen jet directed at the substrate and passing through the ring (Fig. 10). The high voltage between the ring and the target was used to sustain the oxygenated plasma at 0.1-0.5 mTorr of oxygen pressure in the deposition chamber. The hypothesis proposed by Witanachchi et al. (101) was that atomic oxygen both in neutralized and ionized state created in the oxygenated plasma was dynamically introduced in the growing film, leading to the production of as-deposited superconducting films at low substrate temperature. Several groups are now using this laser ablation deposition technique, even though none of them have reported producing as-deposited superconducting films at temperatures as low as 400 °C, as originally claimed by Witanachchi et al. (101). Roas et al. (108), for example, reported the synthesis of as-deposited superconducting films at substrate temperatures in the range 650-780 °C, where, according to the authors, the laser pulsed beam itself seemed to activate the oxygen present in the deposition chamber. Moreover, there has not been a confirmation of the results reported by Witanachchi et al. about the production of as-deposited superconducting films at 400 °C. The data discussed above implies that more systematic work, involving careful measurements of substrate temperature and control deposition parameters, is needed to better understand the underlying mechanism responsible for the observed results, and to reliably establish the limits of the low temperature deposition technique. Initial work in this direction has recently been reported, as discussed below.

Kanai et al. (109) produced as deposited high T_c films on substrates at 480 °C, by laser (ArF, 193 nm) ablation deposition in the presence of a N_2O atmosphere. The reason for using N_2O instead of O_2 for example is because the ArF laser, which fulfilled the double function of ablating the target and activating the oxygen, is much more effective, by about four orders of magnitude, in dissociating N_2O (the absorption cross

section at 193 nm is about 10^{-19} cm² according to Koren et al. (110)) than O₂ (the absorption cross section at 193 nm is about 10^{-23} cm², Koren et al. (110)). The effective dissociation of N₂O results in a substantial amount of activated oxygen, for incorporation into the growing films. This laser-induced oxygen activation effect, has been recently demonstrated in an elegant experiment performed by Koren et al. (110). A Nd-YAG laser was used to ablate a YBa₂Cu₃O_{7-x} target, while an ArF laser beam (directed parallel to the substrate surface) intersected the ablation plume, during the deposition of films either in an O₂ or an N₂O atmosphere. These experiments demonstrated the following:

(a) Films deposited on SrTiO₃ at 600 °C in an O₂ atmosphere, with or without the ArF activation laser, presented a semiconducting behavior without transition to the superconducting state down to 35 K (Fig. 11a), while those deposited in an N₂O atmosphere on similar substrates at the same temperature, with or without the ArF activation laser, showed superconducting transitions with T_c and transition width depending on the particular deposition conditions (Fig. 11b).

(b) The time of arrival of Y, Ba, Cu, and O at the substrate surface is critical for producing films with better superconducting characteristics, i.e., the best films were obtained under conditions that resulted in the simultaneous arrival, at the substrate surface, of species ablated from the target and the activated oxygen (Fig. 11b). The timing of species arrival at the substrate surface was controlled by an appropriate delay between the ArF laser pulse in front of the substrate and the Nd:YAG laser pulse used to ablate the target. The best films were obtained when this delay time coincided with the time of flight of the ablated species between the target and substrate, under the particular background gas pressure conditions (Fig. 11b).

The experimental data described above indicates that the spatial location and formation time of the activated oxygen atoms may be critical to their effective incorporation into the growing film, since atomic species created further away from the substrate may be subjected to a high rate of recombination due to the necessary relatively high pressures in the deposition chamber.

Mizuno et al. (111) used an Ar+O₂ plasma to sputter-deposit polycrystalline Y-Ba-Cu-O films on GaAs (100) having a CaF₂ buffer layer. The substrate temperature was kept at about 450 °C during deposition, and subsequently dropped to 250 °C for 30 minutes followed by a slow cooling in an O₂ atmosphere after deposition, which produced an as deposited high T_c superconducting film, although with a relatively low T_c (45 K). In this case, the activated oxygen was produced by the plasma established between the superconductor target (cathode) and the substrate (anode). A possible reason for the relatively low T_c obtained may have been the bombardment of the growing film by negative oxygen ions and secondary electrons from the target, which can produce deleterious compositional changes as it has been demonstrated by different groups (Rossnagel and Cuomo (12), Terada et al. (27)). These results indicate that not all sources of activated oxygen will be viable alternatives for the production of high quality as deposited superconducting films.

Berkeley et al. (107) explored an alternative method to dynamically introduce oxygen into growing films. They used an ozone jet directed at the substrate to produce as deposited Y-Ba-Cu-O superconducting films. Films deposited at 590 °C and 700 °C presented T_c at 40 K and 80 K respectively.

Electron cyclotron resonance (ECR) sources have been particularly effective in allowing in situ deposition of YBa₂Cu₃O_{7-x}, as demonstrated by Moriwaki et al. (25) and Aida et al. (47). These researchers utilized electron beam evaporation in conjunction with oxygen from an ECR source directed at the substrate. The dominant species in the oxygen plasma near the substrate was identified to be O₂⁺, and the electron temperature estimated (by Langmuir probe) to be ~ 8 eV. The ECR source is also known to yield a

significant concentration of oxygen radicals. Crystalline $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ were produced at substrate temperatures as low as 450 °C.

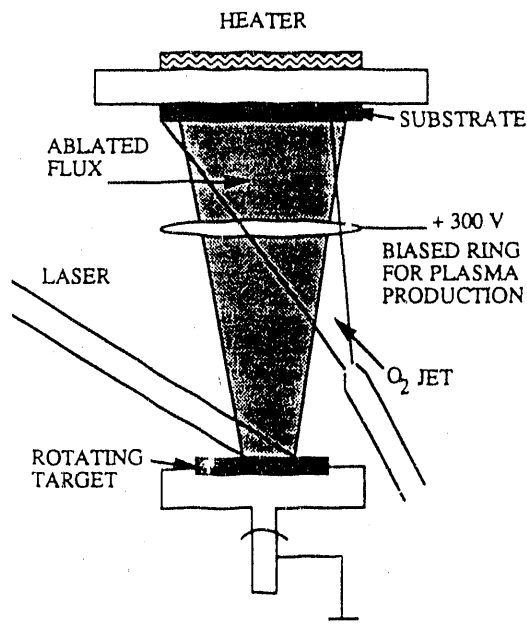


Fig. 10. Schematic of the laser ablation-deposition system used for producing as deposited high T_c superconducting films at low substrate temperature (Witanachchi et al. (101)).

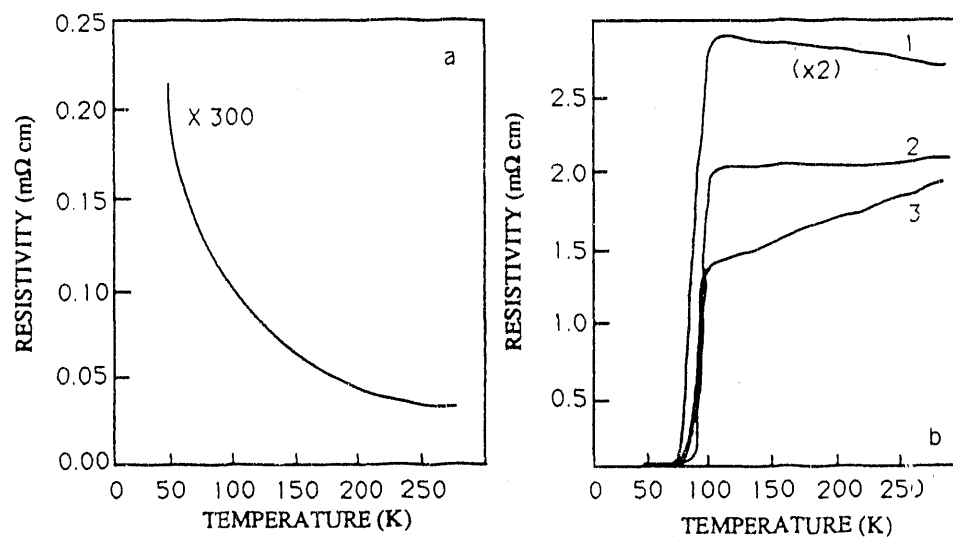


Fig. 11. (a) Resistivity vs. temperature for Y-Ba-Cu-O films deposited on SrTiO₃ at 600 °C in 0.2 Torr of O₂ using a Nd:YAG laser (355 nm, 3.2 J/cm²) to ablate the target, and an ArF (193 nm) excimer laser to irradiate the O₂ gas in front of the target. (b) Same deposition conditions as in (a) but in an N₂O atmosphere; film (1) was deposited without the ArF laser irradiation of N₂O, while (2) and (3) were produced with ArF laser (17 mJ/cm²) irradiation, time delayed with respect to the ablation laser pulse by 1.6 μs and 10 μs respectively (Koren et al. (110)).

Aida et al. (47) also demonstrated that in the case of the evaporation of copper alone, Cu metal is deposited in a molecular oxygen atmosphere (2×10^{-2} Torr) and temperatures as high as 600 °C. This is consistent with the known thermodynamic stability of Cu as a function of oxygen partial pressure. However, CuO has been deposited on substrates even at room temperature in the presence of "active" oxygen originating from an ECR plasma. This study emphasizes the oxidative ability of the ECR plasma and furthermore indicates that additional energy, probably derived from the oxygen ions, can increase the mobility of deposited species on the film surface.

The ECR source has also been used in a novel sputtering geometry by Goto et al. (112). This sputter-deposition method has the advantage that the substrate is not directly exposed to the plasma, which eliminates any possible damage in the film due to bombardment by energetic ions from the plasma.

The studies discussed above indicate that the dynamic incorporation of activated oxygen may be fundamental for producing as-deposited high T_c superconducting films at relatively low substrate temperatures. However, further work is necessary to better understand the complex processes involved in the activated oxygen-assisted deposition of superconducting films, and to control them for producing the high quality films that are necessary for device fabrication.

An important point to be considered, when analyzing data presented in the literature in relation to *in situ* low temperature deposition of high T_c superconducting films, is how the substrate temperature is measured. We have found in our laboratory that measurement of the substrate temperature is not a trivial matter and substantial errors may occur depending on the measuring technique. Unfortunately, the substrate temperatures quoted in the literature may not be accurate in many cases.

PROPERTIES OF FILMS

Fundamental properties of films, such as the transition temperature T_c and transition width, and critical current densities J_c , depend largely on stoichiometry and crystalline structure. These can be affected by film-substrate interactions as well as the substrate crystallography and quality, the latter two including lattice matching to the films, and the type and number of defects, respectively. It is therefore relevant to first consider the substrates that have been used to deposit superconducting films by different techniques, and the film-substrate interactions occurring during deposition and in the subsequent annealing process, when required, before critically discussing the properties of films as synthesized by various techniques.

Substrates and Substrate-Film Interactions

Y-Ba-Cu-O: Many materials have been used as substrates for Y-Ba-Cu-O films, namely: glass, quartz, Si, Al_2O_3 , sapphire, gadolinium gallium garnet (GGG), MgO, $2MgO \cdot SiO_2$, Ytria stabilized cubic ZrO_2 , BaF_2 , $BaTiO_3$, Ti_9O_{20} , $SrTiO_3$, Sr_2TiO_4 , $LaGaO_3$, and $LaAlO_3$. High quality films have been obtained using many of these substrates, especially those having good lattice matching with the film, such as $SrTiO_3$, $LaAlO_3$, and $LaGaO_3$. For example, films exhibiting $T_c \geq 70$ K have been synthesized on sapphire (Hong et al. (8), Scheuermann et al. (53)), MgO (Aida et al. (47), Adachi et al. (24), Cucmo et al. (113), Burbidge et al. (62)), ZrO_2 (Cuomo et al. (113), Bruyere et al. (37), Wiesmann et al. (59)), BaF_2 (Cuomo et al. (113), Yee et al. (114)), $BaTiO_3$ (Lee et al. (115)), Si (Lee et al. (115)), $LaGaO_3$ (Sandstrom et al. (116)), $LaAlO_3$ (Simon et al. (117)), and $LiNbO_3$ (Hohler et al. (140)).

A strong interdiffusion of elements at the film-substrate interface can occur because of the relatively high temperatures involved. For example, glass, quartz, Si, and GGG, are

reactive substrates, and $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films deposited on them have generally not shown superconductivity after a high temperature anneal (Aida et al. (47), Houdy et al. (118), Lin et al. (55)). This is often due, to a large extent, to a strong reactive segregation of different film components. For example, films deposited on Si have shown a strong concentration of Y on the surface, Ba in the middle, and Cu rich layers at the film-substrate interface (Lee et al. (9)). On the other hand, annealing of films deposited on quartz resulted in Cu, Y, and Cu rich layers at the surface, middle, and film-substrate interface layers, respectively; Ba in these films penetrated into the substrate and only a small amount was retained in the films.

In relation to substrate diffusion into the films, the transport of Si from quartz into $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ appears to be stronger than that of Al from sapphire or Mg from MgO (Nakajima et al. (119)). However, more systematic work is necessary to elucidate some apparent inconsistencies regarding results from different groups. For example, contrary to the strong diffusion of Si observed by Nakajima et al. (119), other researchers (Lee et al. (115)) have recently claimed that they succeeded in producing as-deposited Y-Ba-Cu-O superconducting films on Si at temperatures in the range 600-700 °C. They indicated that no significant diffusion of Si from the substrate into the film was observed at temperatures ≤ 650 °C. Also, post-deposition RTA has yielded superconducting Y-Ba-Cu-O films on Si and SiO_2 substrates (Aslam et al. (120)), and no diffusion of Si into the films was observed.

Polycrystalline and single crystal Al_2O_3 (sapphire) have also been used as substrates. Film-substrate reactions have been observed for Y-Ba-Cu-O films at temperatures above 700 °C with the interfacial formation of BaAl_2O_4 . Films with non-superconducting properties or low T_c have been produced on both amorphous and polycrystalline alumina (Makous et al. (10), Shah and Carcia (11), Cuomo et al. (113), Lanchbery (46), Bao et al. (83), Tsaur et al. (84)). Auger electron spectroscopy (AES) sputter-depth profile analysis has shown that annealed films on alumina tend to have several layers, i.e., the surface contains Ba, Cu and excess Y, followed by intermediate Y, Ba, and Cu rich layers. Additionally, enhanced concentrations of Ba and Al have been observed at the film-substrate interface suggesting the formation of aluminates. An additional problem related to the interaction of Al_2O_3 substrates with 123 films is the tendency of Al to enhance the formation of the tetragonal non-superconducting phase even if present in small amounts (Hu et al. (39)). The substrate temperature is particularly critical in controlling the characteristics of films deposited on alumina, as it has been demonstrated for 123 films. For films on sapphire, the resistivity decreased when the substrate temperature was reduced from 900 °C to 770 °C, most probably because of a reduced film-substrate interaction. However, the film resistivity increased for annealing temperatures < 770 °C due to incomplete formation of the orthorhombic 123 phase (Stamper et al. (121)).

High quality films have been grown on ZrO_2 , MgO, and particularly on SrTiO_3 , with the highest reported values of T_c being in the range 80-90 K (Liou et al. (122), de Vries et al. (123)). These three substrates are generally less reactive than Al_2O_3 , Si, or SiO_2 . However, interface analyses have shown that Mg, Zr, Sr, and Ti still diffuse into Y-Ba-Cu-O films (Cuomo et al. (113), Houdy et al. (118), and Nakajima et al. (119)). However, these elements appear to have less effect in relation to suppressing superconductivity in the films, particularly Sr, which substitutes Y in the orthorhombic phase.

LaGaO_3 and LaAlO_3 have been investigated as substrate candidates mainly because of their favorable dielectric properties, which make them good candidates for applications in certain high frequency devices. These substrates also present a good lattice and thermal expansion match to $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. Many groups have obtained good results with these substrates. Some other recently reported candidates as substrates for microwave

applications include SrLaAlO₄ (Brown et al.(124)) and CaNdAlO₄ (Berkowski et al.(125)).

Bi and Tl compounds: In general, these films are deposited on similar substrates as the YBa₂Cu₃O_{7-x} films. For example, Bi-Sr-Ca-Cu-O films have been successfully deposited (using various techniques) on MgO (Sugimoto et al.(126), Hakuraku et al.(44), and Sullivan et al.(127)), SrTiO₃ (Eckstein et al.(128) and Chen et al.(41)), and LaGaO₃ (Chen et al.(41)), to name a few. Some examples of substrates successfully used for Tl-Ba-Ca-Cu-O film growth include MgO and SrTiO₃ (Lee et al.(129), Hong et al.(18)), ZrO (Lee (129)), and LaAlO₃ (Subramanyam et al.(45) and Hammond et al.(130)).

Buffer Layers

Some of the more technologically feasible substrates, such as Si, interdiffuse with the superconducting layer. Therefore, researchers have tried to minimize or eliminate that interaction by depositing a buffer layer on top of the substrate. There is also often a need to deposit films on conducting surfaces, which can be achieved by the use of conducting buffer layers. Buffer layers investigated until now include: Cu, Ag, Au, Pt, Nb, Ni, Ti, Vn, NbN, MgO, Y₂O₃, SiO₂, TiO₂, ZrO₂, Ta₂O₅, RuO₂, SrTiO₃, BaTiO₃ and MgAl₂O₄ (Lee et al. (9), Makous et al. (10), Hu et al. (39), Gurvitch and Fiory (50), Miura et al. (54), Burbidge et al. (62), Stamper et al. (121), Jia and Anderson (131), and Wu et al. (141), Berezin et al. (142), Yi et al. (143)). Desirable characteristics of a buffer layer include: (a) chemical inactivity, (b) barrier against film-substrate species interdiffusion, (c) lattice matching to substrate, for epitaxial growth of both the buffer layer and the 123 film.

Ag, Au, and Nb buffer layers have been used to improve the superconducting properties of YBa₂Cu₃O_{7-x} films, and successful substrate/buffer combinations reported in the literature include ZrO₂/Ag, MgO/Nb, MgO/Ag, and MgO/Au. Myoren et al.(132) have shown that high quality YBa₂Cu₃O_{7-x} can be obtained on Si(100) using a yttria-stabilized zirconia (YSZ) buffer, and use of a Y₂O₃/YSZ bilayer buffer on Si produced films with a J_c(77 K) of 1x10⁶ A/cm². Another interesting buffer layer enabling sputter deposition of YBa₂Cu₃O_{7-x} on Si is RuO₂ (Jia and Anderson (131)). They achieved films with zero resistance at 79K using a deposition temperature of only 500 °C. Although these films are polycrystalline and not highly oriented, this is a very promising result (one must, however, be wary of reported substrate temperatures).

Noble metals have also been used as buffer layers for Bi-Sr-Ca-Cu-O films. Silver has shown to be a promising buffer material, although the use of Au and Pt proved unsuccessful (Matthiesen et al.(133)). In general, more work is needed to better understand the behavior of the various buffer layers, and how their properties are affected by changes in deposition conditions.

Properties of Sputter-Deposited Films

Sputter-deposited films of all classes of the high-T_c compounds have generally exhibited a strong texture. Nearly epitaxial grown films, with the c and/or a-axes parallel to the substrate surface, have been obtained after high temperature annealing (about 900 °C) on (100) SrTiO₃ substrates (Hirochi et al. (134), and Sandstrom et al. (26)). YBa₂Cu₃O_{7-x} films deposited on (100) SrTiO₃ have shown a-axis orientation perpendicular to the substrate when deposited at rather low substrate temperatures (~700 °C), with the orientation shifting to c-axis growth at higher substrate temperatures, around 800 °C (Geerk et al.(29)). On the other hand, films synthesized on (110) SrTiO₃ have shown a crystalline texture such that the c-axis of each crystal is oriented parallel to one of the three <100> directions of the (110) substrate, near the interface. Additionally,

highly oriented (c-axis perpendicular to the substrate surface) Y-Ba-Cu-O films have been produced on MgO, ZrO₂, BaF₂, LaAlO₃ and LaGaO₃ substrates and on oriented Pt buffer layers on Al₂O₃ substrates (Adachi et al. (24), Yee et al. (114), Terada et al. (27), Tanaka and Itozaki (135), Hatta et al. (136), Wiesmann et al. (59), Sandstrom et al. (116), Simon et al. (117).

Because the high temperature superconductors are anisotropic, the film orientation will influence the observed electrical properties. For example, the J_c (4.2K) of YBa₂Cu₃O_{7-x} may be $>10^7$ A/cm² along the a-b plane, while being only 10^4 to 10^5 A/cm² along the c direction (Braginski et al.(137)). Highly oriented (c-axis) sputter deposited films obtained recently by Myoren et al.(132) on Si (topped with a Y₂O₃/YSZ buffer layer) exhibited J_c 's of 1×10^7 at 4.2 K and 1×10^6 A/cm² at 77 K. Randomly oriented Y-Ba-Cu-O films, on the other hand, have exhibited J_c values in the range 10^5 - 10^6 A/cm² at 4.2 K and 10^3 - 10^4 A/cm² at 77 K (Silver et al. (51), Shah and Carcia (11)). Possibly the highest J_c measured on sputter-deposited films of the Y-Ba-Cu-O class of compounds is 2.54×10^6 A/cm² at 77 K, which has been achieved in a highly oriented (001) HoBa₂Cu₃O_{7-x} film deposited on a (001) MgO substrate (Tanaka and Itozaki (135)). A J_c of about 1.5×10^6 A/cm² was maintained in this film even when exposed to a magnetic field of 1.0 T. Other workers have recently demonstrated films having J_c 's of 1×10^6 A/cm² at magnetic fields as high as 7 Tesla (Qiu et al.(138)). In general, the highest quality films (high T_c , J_c , and smooth surfaces) have been obtained using the *in situ* deposition route, avoiding high temperature anneals.

Highly oriented (c-axis) sputtered films of the bismuth and thallium compounds have also been produced, having high J_c 's as well. Tl₂Ba₂Ca₂Cu₃O₁₀ films deposited on SrTiO₃, having a T_c of 116 K, have a J_c ($T_c = 100$ K) of 1×10^5 A/cm² (Hong et al.(18)). However, these films are post-processed using a high temperature anneal. Bi-Sr-Ca-Cu-O films containing mixtures of the Bi₂Sr₂CaCu₂O₈ and Bi₂Sr₂Ca₂Cu₃O₁₀ phases ($T_c = 81$ K) show J_c 's of 3×10^6 A/cm² at 4.2 K, and 8×10^4 A/cm² at 77 K (Hakuraku et al.(44)). Highly oriented Bi₂Sr₂Ca₂Cu₃O₁₀ films, containing many intergrowth layers (excess, or lack of, CuO planes periodically) have been obtained having a T_c of 95 K and a J_c (77 K) of 3.4×10^6 A/cm² (Itozaki et al.(139)).

Sputter-deposited films have generally shown sharp transitions to zero resistivity. However, a sharp transition should not be interpreted as indicative of a film containing only the superconducting phase. A few percent of the superconducting phase is enough to produce a sharp transition, provided that the grains are in contact with each other. Meissner effect measurements are necessary to determine the total fraction of the superconducting phase in a film. Very few Meissner effect measurements have been reported for sputter-deposited films until now, many of which have shown wide transitions. However, the highly oriented films having large J_c 's are evidently very homogeneous, although generally only resistive measurements have been performed.

CONCLUSIONS

A limited review has been presented here on sputter-deposition techniques for production of high T_c superconducting films. Recent results show that high quality films can be obtained, even on Si substrates with the use of proper buffer layers. The use of sputter deposition has proved feasible for the growth of *in situ* films of both Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O compounds at moderate substrate temperatures. However, much work is still needed to understand many of the basic processes occurring during film deposition. This understanding is fundamental for achieving the necessary control in film synthesis, which will lead to applications in device fabrication. Outstanding issues that need to be addressed are:

(1) Control of the uniformity of film composition and thickness across extended areas. This is critical for the integration of high T_c superconducting films with the current microelectronics technology.

(2) Production of as-deposited superconducting films at the lowest possible substrate temperature. This is also critical for the integration of these films with the current microelectronics technology mainly based on silicon.

(3) Integration of the deposition techniques with patterning methods for the fabrication of devices based on high T_c superconducting films. In relation to this issue, much work is also needed to develop and optimize patterning techniques, although some work has already been done on this topic.

Given the pace at which research on high T_c superconducting films has been developing, relevant advances can be expected in the near future.

ACKNOWLEDGMENTS

The authors would like to acknowledge the support from DARPA (N-00014-88-K-0525), NSF (DMC-8813502, DMR-88-07367), ONR (N-00014-88-K-1526), and DOE (Basic Energy Sciences W-31-109-Eng-38 and DE-FG05-88ER-45359).

REFERENCES

1. Bednorz, J. G. and Muller, K. A., *Zeitschrift für Physik* vol. **B64**, p. 189, (1986).
2. Wu, M. K., Ashburn, L. J., Torng, C. J., Hor, P. H., Meng, R. L., Gao, L., Huang, Z., Wang, J. Y. Q., and Chu, C. W., *Physical Review Letters*, vol. **58**, p. 908, (1987).
3. Maeda, H., Tanaka, T., Fukutomi, M. and Asano, T., *Japanese Journal of Applied Physics*, vol. **27**, L209, (1988).
4. Sheng, Z. Z. and Hermann, A. M., *Nature*, vol. **332**, p. 138, (1988).
5. Harper, J. M. E., Colton, R. J., and Feldman, L. C. (Eds.), *American Institute of Physics Conference Proceedings "Thin Film Processing and Characterization of High Temperature Superconductors"*, No. **165**, (1988).
6. May, P., Jedamzik, D., Boyle, W., and Miller, P., *Superconducting Science Technology*, vol. **1**, p. 1, (1988).
7. Auciello, O., Krauss, A.R., Kingon, A.I. and Ameen, M.S., *Scanning Microscopy*, vol. **4**, p. 203, (1990).
8. Hong, M., Liou, S., Kwo, H.J., and Davidson, B.A., *Applied Physics Letters*, vol. **51**, p. 694, (1987).
9. Lee, S. Y., Murdock, B., Chin, D., and Van Duzer, T., *American Institute of Physics Conference Proceedings "Thin Film Processing and Characterization of High Temperature Superconductors"*, Harper, J. M. E., Colton, R. J., and Feldman, L. C. (Eds.), No. **165**, p. 427, (1987).
10. Makous, J. L., Maritato, L., Falco, C. M., Cronnin, J. P., Rajendran, G. P., Uhlmann, E. V. and Uhlmann, D. R., *Applied Physics Letters*, vol. **51**, p. 2164, (1987).

11. Shah , S. I. and Carcia, P. F., American Institute of Physics Conference Proceedings "Thin Film Processing and Characterization of High Temperature Superconductors", Harper , J. M. E., Colton , R. J. and Feldman, L. C. (Eds.), No. 165, p. 50, (1988).
12. Rossnagel, S. M. and Cuomo, J. J., American Institute of Physics Conference Proceedings "Thin Film Processing and Characterization of High Temperature Superconductors", Harper, J. M. E., Colton , R. J. and Feldman , L. C. (Eds.), No. 165, p. 106, (1988).
13. Shah, S. I., Thin Solid Films, vol. 181, p.157, (1989).
14. Subramanyam, G., Radpour, F., Kapoor, V. J., and Lemon, G. H., Journal of Applied Physics, vol. 68, p. 1157, (1990).
15. Thornton, J. A., in "Semiconductor Materials and Process Technology Handbook", McGuire, G. E. (Ed.), Noyes Publications, Park Ridge, NJ, pp. 329, (1988).
16. Auciello, O. and Krauss, A. R., Proceedings 3rd International Symposium on Surface Science, Salzburg, Austria (reprints available from O. Auciello), pp. 197, (1988).
17. Betz, G. and Wehner, G. K., Sputtering of Multicomponent Materials, in "Sputtering by Particle Bombardment, II", Ch.2, Berisch, R. (Ed.), Springer Verlag, pp. 11, (1981).
18. Hong, M., Liou, S. H., Bacon , D. D., Grader , G. D., Kwo , J., Kortan , A. R., and Davidson, B. A., Applied Physics Letters, vol. 53, p. 2102, (1988).
19. Auciello , O., Athavale , S., Hankins , O. E., Sito , M., Schreiner, A. F. and Biunno, N., Applied Physics Letters, vol. 53, p. 72, (1988).
20. Kang , J. H., Kampwirth , R. T., Gray , K. E., Marsh , S. and Huff, E. A., Physics Letters, vol. A128, p. 102, (1988).
21. Kang , J. H., Kampwirth , R. T., and Gray, K. E., Physics Letters, vol. A131, p. 208, (1988).
22. Kang, J. H., Kampwirth, R. T., and Gray, K. E., Applied Physics Letters, vol. 52, p. 2080, (1988).
23. Klein, J. D., Yen, A., and Clauson, S. L., Applied Physics Letters, vol. 56, p. 394, (1989).
24. Adachi , H., Hirochi , K., Setsune , K., Kitabatake , M., and Wasa, K., Applied Physics Letters, vol. 51, p. 2263, (1987).
25. Moriwaki , K., Enamoto , Y., Kubo , S. and Murakami, T., Japanese Journal of Applied Physics, vol. 27, L2075, (1988).
26. Sandstrom, R. L., Gallagher, W. J., Dinger, T. R., Koch, R. H., Laibowitz, R.H., Kleinsasser, R.B., Gambino, R. J., Bumble, B., and Chisholm, M. F., Applied Physics Letters, vol. 53, p. 444, (1988).
27. Terada, N., Ihara, H., Jo, M., Hirabayashi, M., Kimura, Y., Matsutani, K., Hirata, K., Ohn, E., Sugise, R., and Kawashima, F., Japanese Journal of Applied Physics, vol. 27, L639, (1988).

28. Auciello, O., Athavale, S., Bourham, M., Hankins, O. E., Gras-Marti, A., and Valles-Abarca, J. A., Vacuum (in press, 1990).
29. Geerk, J., Linker, G., and Meyer, O., Materials Science Reports, vol. 4, p. 193, (1989).
30. Bullock, D. C., Rettner, C. T., Lee, V. Y., Lim, G., Savoy, R. J. and Auerback, D. J., American Institute of Physics Conference Proceedings "Thin Film Processing and Characterization of High Temperature Superconductors," Harper, J. M. E., Colton, R. J., and Feldman, L. C. (Eds.), No. 165, p. 71, (1987).
31. Michikami, O., Asano, H., Katoh, Y., Kubo, S., and Tanabe, K., Japanese Journal of Applied Physics, vol. 26, L1199, (1987).
32. Ohkuma, H., Mochiku, T., Kanke, Y., Wen, Z., Yokoyama, S., Japanese Journal of Applied Physics, vol. 26, L1484, (1987).
33. Han, Z., Bourget, L., Li, H., Ulla, M., Millman, W. S., Baum, H. P., Xu, M. F., Sarma, B. K., Levy, M., and Tonner, B. P., American Institute of Physics Conference Proceedings, "Thin Film Processing and Characterization of High Temperature Superconductors", Harper, J. M. E., Colton, R. J., Feldman, L. C. (Eds.), No. 165, p. 66, (1987).
34. Enamoto, Y., Murakami, T., Suzuki, M., and Moriwaki, K. Japanese Journal of Applied Physics, vol. 26, L1248, (1987).
35. Kamada, T., Setsune, K., Hirao, T., and Wasa, K., Applied Physics Letters, vol. 52, p. 1726, (1988).
36. Mochiku, T., Kanke, Y., Wen, Z., Iguchi, Y., and Yamaka, Y., Japanese Journal of Applied Physics, vol. 27, L1679, (1988).
37. Bruyere, J. C., Marcus, J., Reydet, P. L., Escribe-Fillipini, and Schlenker, C., Materials Research Bulletin, vol. 23, p. 429, (1988).
38. Onuma, Y., Kamimura, K., Nkao, M., Kunugi, K., and Kubota, M., Japanese Journal of Applied Physics, vol. 27, p. 1351, (1988).
39. Hu, R., Jiang, C., and Luo, H. L., Materials Research Bulletin, vol. 23, p. 1159, (1988).
40. Gawalek, W., Michalke, W., Bruchlos, H., Eick, T., Hergt, R., and Schmidt, G., Physica Status Solidi, vol. A109, p. 503, (1988).
41. Chen, J., and Chow, L., Solid State Communication, vol. 74, p. 1095, (1990).
42. Tseng, M. R., Chu, J. J., Huang, Y. T., Wu, P. T., and Wang, W. N., Journal of Applied Physics, vol. 67, p. 2657, (1990).
43. Lin, S. L., Tien, C., Chin, T. S., Huang, T. W., and Hung, M. P., Japanese Journal of Applied Physics, vol. 29, p. L775, (1990).
44. Hakuraku, Y., Higo, S., and Ogushi, T., Applied Physics Letters, vol. 57, p. 925, (1990).

45. Subramanyam, G., Radpour, F., and Kapoor, V., *Journal of Applied Physics*, vol. 56, p. 1799, (1990).
46. Lanchbery, J. F., *Journal of Physics*, vol. D21, p. 538, (1988).
47. Aida, T., Tsukamoto, A., Imagawa, K., Fukazawa, T., Sato, S., Shindo, K., Takagai, K., and Miyauchi, K., *Japanese Journal of Applied Physics*, vol. 28, L635, (1989).
48. Ginley, D. S., Kwak, J. F., Hellmer, R. P., Baughman, R. J., Venturini, E. L., and Morosin, B., *Applied Physics Letters*, vol. 53, p. 406, (1988).
49. Blamire, M. G., Morris, G. W., Someckh, R. E., and Evetts, J. E., *Journal of Physics*, vol. D20, p. 1330, (1987).
50. Gurvitch, M., and Fiory, A. T., *Applied Physics Letters*, vol. 51, p. 1027, (1987).
51. Silver, R. M., Talvacchio, J., and Lozanne, A. L., *Applied Physics Letters*, vol. 51, p. 2149, (1987).
52. Face, D. W., Neal, M. J., Matthiesen, M. M., Kucera, J. T., Crain, J., Graybeal, J., Orlando, M. T. P., and Rudman, D. A., *Applied Physics Letters*, vol. 53, p. 246, (1988).
53. Scheuermann, M., Chi, C. C., Tsuei, C. C., Yee, D. S., Cuomo, J. J., Laibowitz, R. B., *Applied Physics Letters*, vol. 51, p. 1951, (1987).
54. Miura, S., Terashima, Y., Sagoi, M., and Kubo, K., *Japanese Journal of Applied Physics*, vol. 27, L1260, (1988).
55. Lin, R. J., Chen, Y. C., Kung, J. H., and Wu, P. T., *Materials Research Society Symposium Proceedings "High Temperature Superconductors"*, Brodsky, M. B., Dynes, R. C., Kitazawa, K., and Tuller, H. L. (Eds.), vol. 99, p.319, (1988).
56. Li, H. C., Linker, G., Ratzel, F., Smithey, R., and Geerk, J., *Applied Physics Letters*, vol. 52, p. 1098, (1988).
57. Bormann, R. and Nolting, J., *Applied Physics Letters*, vol. 54, p. 2148, (1989).
58. Hammond, R. H., and Bormann, R., *Physica C*, vol. 162-164, p. 703, (1989).
59. Wiesmann, H., Chen, D. H., Sabatini, R. L., Hurst, J., Ochab, J., Ruckman, M. W., *Journal of Applied Physics*, vol. 65, p.1644, (1989).
60. Eom, C. B., Sun, J. Z., Yamamoto, K., Marshall, A. F., Luther, K. E., Geballe, T. H., and Laderman, S.S., *Applied Physics Letters*, vol. 55, p. 595, (1989).
61. Kleinand, J. D., and Yen, A., *Journal of Vacuum Science and Technology*, vol. A 8, p. 1, (1990).
62. Burbidge, D., Mulhern, P., Dew, S., and Parsons, R., *American Institute of Physics Conference Proceedings "Thin Film Processing and Characterization of High Temperature Superconductors"*, Harper, J. M. E., Colton, R. J., and Feldman, L. C. (Eds.), No. 165, p. 87, (1987). Liang, J. K., Zhang, Y. L., Huang, J.Q., Xie, S. S., Che, G. C., Chen, X. R., Ni, Y. M., Zhen, D. N., and Jia, S. L., *Physica C*, vol. 156, p. 616, (1988).

63. Whener, G., Kim, Y. H., Kim, D. H., and Goldman, A. M., *Applied Physics Letters*, vol. 52, p. 1187, (1988).
64. Akune, T., and Sakamoto, N., *Japanese Journal of Applied Physics*, vol. 27, L2078, (1988).
65. Wu, X. D., Muenchausen, R. E., Foltyn, S., Estler, R. C., Dye, R. C., Garcia, A. R., Nogar, N. S., England, P., Ramesh, R., Hwang, D. M., Ravi, T. S., Chang, C. C., Venkatesan, T., Xi, X. X., Li, Q., and Inam, A., *Applied Physics Letters*, vol. 57, p. 523, (1990).
66. Kobrin, P. H., DeNatale, J. F., Housley, R. M., Flintoff, J. F., and Harber, A. B., *Advanced Ceramic Materials*, vol. 2, p. 430, (1987).
67. Gao, J., Zhang, Y. Z., Zaho, B. R., Out, P., Yuan, C. W., and Li, L., *Applied Physics Letters*, vol. 53, p. 2675, (1988).
68. Auciello, O., and Krauss, A. R., *American Institute of Physics Conference Proceedings "Thin Film Processing and Characterization of High Temperature Superconductors"*, Harper, J. M. E., Colton, R. J., Feldman, L.C. (Eds.), No. 165, p. 114, (1989).
69. Krauss, A. R., and Auciello, O., U.S. Patent No 4,923,585 (1990).
70. Krauss, A. R., Auciello, O., Kingon, A. I., Ameen, M. S., Barr, T., and Liu, Y. L., *Review Scientific Instrument*, in press, (1990).
71. Ameen, M. S., Graetinger, T. M., Auciello, O., Rou, S. H., Kingon, A. I., and Krauss, A. R., *Materials Research Society Symposium Proceedings*, vol. 152, p. 175, (1989).
72. Kaufman, H. R., Cuomo, J. J., and Harper, J. M. E., *Journal of Vacuum Science and Technology*, vol. 21, p. 725, (1982).
73. Mahoney, J. F., Pereel, J., and Forrester, A. T., *Applied Physics Letters*, vol. 38, p. 320, (1981).
74. Ameen, M. S., Auciello, O., Rou, S. H., Soble, C. S., Graetinger, T. M., Krauss, A. R., and Kingon, A. I., *American Institute of Physics Conference Proceedings "High T_c Superconducting Thin Films: Processing, Characterization, and Applications"*, Stockbauer, R. L., Krishnaswamy, S. V., and Kutz, R. L. (Eds.), No. 200, p. 79, (1990).
75. Krauss, A.R., Auciello, O., Kingon, A.I., Ameen, M.S., Liu, Y.L., Barr, T., Graetinger, T.M., Rou, S.H., Soble, C.S., and Gruen, D.M., *Proceedings of the European Materials Research Society Spring Meeting*, in press, (1990).
76. Biersack, J.P., and Haggmark, L.G., *Nuclear Instruments and Methods*, vol. 174, p. 257, (1980).
77. Auciello, O., Ameen, M.S., Krauss, A.R., Kingon, A.I., and Ray, M.A., *Materials Research Society Conference Proceedings*, in press, (1990).
78. Tarascon, J.M., McKinnon, W.R., Greene, L.H., Hull, G.W., Bagley, B.G., and Vogel, V.G., *Advances in Ceramic Materials*, vol. 2, p. 498, (1987).

79. Asano, H., Tanabe, K., Katoh, Y., Kubo, S., and Michikami, O., *Japanese Journal of Applied Physics*, vol. 26, p. L1221, (1987).
80. Dam, E., Baller, T.S., van Veen, G.N.A., van Hal, H.A.M., de Vries, J.W.C., and Stollman, G.M., *Materials Research Society Symposium Proceedings, "High Temperature Superconductors"*, Brodsky, M.B., Dynes, R.C., Kitazawa, K., and Tuller, H.L. (Eds.), vol. 99, p. 319, (1988).
81. Hayashi, S., Kamada, T., Setsune, K., Hirao, T., Wasa, K., and Matsuda, A., *Japanese Journal of Applied Physics*, vol. 27, p. L1257, (1988).
82. Naito, M., Hammond, R.H., Oh, B., Hahn, M.R., Hsu, J.W.P., Rosenthal, P., Marshall, A.F., Beasley, M.R., Geballe, T.H., and Kapitulnik, A.J., *Materials Research*, vol. 2, p. 713, (1987).
83. Bao, Z.L., Wang, F.R., Yiang, Q.D., Wang, S.Z., Ye, Z.Y., Wu, K., Li, C.Y., and Yin, D.L., *Applied Physics Letters*, vol. 51, p. 946, (1987).
84. Tsauro, B.Y., DiIorio, M.S., and Strauss, A.J., *Applied Physics Letters*, vol. 51, p. 858, (1987).
85. Lathrop, D.K., Russek, S.E., and Buhrman, R.A., *Applied Physics Letters*, vol. 51, p. 1554, (1987).
86. Chan, S., Greene, L.H., Feldman, W.L., Miceli, P.F., and Bagley, B.G., *American Institute of Physics Conference Proceedings, "Thin Film Processing and Characterization of High Temperature Superconductors"*, Harper, J.M.E., Colton, R.J., and Feldman, L.C., (Eds.), No. 165, p. 28, (1987).
87. Qiu, C.X., and Shih, I., *Applied Physics Letters*, vol. 52, p. 587, (1988).
88. Mogro-Campero, A., Hunt, B.D., Turner, L.G., Burrel, M.C., and Balz, W.E., *Applied Physics Letters*, vol. 52, p. 584, (1988).
89. Terashima, T., Ijima, K., Yamamo, K., Bando, Y., and Mazaki, H., *Japanese Journal of Applied Physics*, vol. 27, p. L91, (1988).
90. Berberich, P., Tate, J., Dietsche, W., and Kinder, H., *Applied Physics Letters*, vol. 53, p. 925, (1988).
91. Chang, C., Tsuei, C. C., Chi, C.C., and McGuire, T.R., *Applied Physics Letters*, vol. 52, p. 72, (1988).
92. Liou, S.H., Hong, M., Davidson, B.A., Farrow, R.C., Kwo, J., Hsieh, T.C., Fleming, R.M., Chen, H.S., Feldman, L.C., Kortan, R.A., and Felder, R.J., *American Institute of Physics Conference Proceedings, "Thin Film Processing and Characterization of High Temperature Superconductors"*, Harper, J.M.E., Colton, R.J., and Feldman, L.C., (Eds.), No. 165, p. 79, (1987).
93. Ma, L.Y., Licata, T.J., Wu, X., Yang, E.S., and Chang, C., *Applied Physics Letters*, vol. 53, p. 2229, (1988).
94. Lee, S.J., Rippert, E.D., Jin, B.Y., Song, S.N., Hwu, S.J., Poppelmeier, K., and Ketterson, J.B., *Applied Physics Letters*, vol. 51, p. 1194, (1987).
95. Aslam, M., Soltis, R.E., Logothetis, E.M., Ager, R., Mikkor, M., Win, H., Chen, J.T., and Wenger, L.E., *Applied Physics Letters*, vol. 53, p. 153, (1988).

96. Dhere, N.G., *Vacuum*, vol. 40, p. 263, (1990).
97. Guarnieri, C.R., Roy, R.A., Saenger, K.L., Shivashankar, S.A., Yee, D.D., and Cuomo, J.J., *Applied Physics Letters*, vol. 53, p. 532, (1988).
98. Osborne, N.R., Dew, S.K., Mulhern, P.J., and Parsons, R.P., *Thin Solid Films*, vol. 181, p. 165, (1989).
99. Cooke, D.W., Gray, E.R., Arendt, P.N., Reeves, G.A., Houlton, R.J., Elliott, N.E., and Brown, D.R., *Applied Physics Letters*, vol. 56, p. 2147, (1990).
100. Wasa, K., Kitabatake, M., Azachi, H., Setsune, K., and Hirochi, H., *American Institute of Physics Conference Proceedings, "Thin Film Processing and Characterization of High Temperature Superconductors"*, Harper, J.M.E., Colton, R.J., and Feldman, L.C., (Eds.), No. 165, p. 38, (1988).
101. Witanachchi, S., Kwok, H.S., Wang, X.W., and Shaw, D.T., *Applied Physics Letters*, vol. 53, p. 234, (1988).
102. Witanachchi, S., Patel, S., Kwok, H.S., and Shaw, D.T., *Applied Physics Letters*, vol. 54, p. 578, (1989).
103. Margaritondo, G., Joynt, R., and Onellion, M., (Eds.), *American Institute of Physics Conference Proceedings, "High T_c Superconducting Thin Films, Devices, and Applications"*, No. 182, (1989).
104. Kwo, J., Hsieh, T.C., Flemming, R.M., Hong, M., Liou, S.H., Davidson, B.A., and Feldman, L.C., *Physical Review*, vol. B36, p. 4039, (1987).
105. SPIE-Int. Soc. Opt. Eng. (USA), "High T_c Superconductivity: Thin Films and Devices," vol. 948, (1988).
106. Miura, S., Yoshitake, T., Matsubara, S., Miyasaka, Y., Shohata, N., Satoh, T., *Applied Physics Letters*, vol. 53, p. 1967, (1988).
107. Berkeley, D.D., Johnson, B.R., Anand, N., Beauchamp, K.M., Conroy, L.E., Golman, A.M., Maps, J., Mauersberger, K., Mecartney, M.L., Morton, J., Touminen, M., and Zhang, Y.Y.-J., *Applied Physics Letters*, vol. 53, p. 1973, (1988).
108. Roas, B., Schultz, L., and Endres, G., *Applied Physics Letters*, vol. 53, p.1557, (1988).
109. Kanai, M., Kawai, T., Kawai, S., and Tabata, H., *Applied Physics Letters*, vol. 54, p. 1802, (1989).
110. Koren, G., Gupta, A., and Baseman, R.J., *Applied Physics Letters*, vol. 54, p. 1920, (1989).
111. Mizuno, K., Miyauchi, M., Setsune, K., and Wasa, K., *Applied Physics Letters*, vol. 54, p. 383, (1989).
112. Goto, T., Masumoto, M., and Toshio, H., *Japanese Journal of Applied Physics*, vol. 28, p. L88, (1989).

113. Cuomo, J.J., Chisholm, M.F., Yee, D.E., Mikalsen, D.J., Madakson, P.B., Roy, R.A., Giess, E., and Scilla, G., American Institute of Physics Conference Proceedings, "Thin Film Processing and Characterization of High Temperature Superconductors", Harper, J.M.E., Colton, R.J. and Feldman L.C. (Eds.), No. 165, p. 141, (1987).
114. Yee, D.S., Gambino, R.J., Chisholm, M.F., Cuomo, J.J., Madakson, P.B., and Karasinski, J., American Institute of Physics Conference Proceedings, "Thin Film Processing and Characterization of High Temperature Superconductors", Harper, J.M.E., Colton, R.J., and Feldman, L.C., (Eds.), No. 165, p. 132, (1987).
115. Lee, W.Y., Salem, J., Lee, V., Retter, C.T., Lim, J., Savoy, R., and Deline, V., American Institute of Physics Conference Proceedings, "Thin Film Processing and Characterization of High Temperature Superconductors", Harper, J.M.E., Colton, R.J., and Feldman, L.C., (Eds.), No. 165, p. 95, (1987).
116. Sandstrom, R.L., Giess, E.A., Gallagher, W.J., Segmuller, A., Cooper, E.I., Chisholm, M.F., Gupta, S., Shinde, S., and Laibowitz, R.B., Applied Physics Letters, vol. 53, p. 1874, (1988).
117. Simon, R.W., Platt, C.E., Lee, A.E., Lee, G.S., Daly, K.P., Wire, M.S., Luine, J.A., and Urbanik, M., Applied Physics Letters, vol. 53, p. 2677, (1988).
118. Houdy, P., Sirat, J.A., Theeten, J.B., Landesman, J.P., Baudry, H., Monneraye, M., Schiller, C., and Patillon, J.N., American Institute of Physics Conference Proceedings, "Thin Film Processing and Characterization of High Temperature Superconductors", Harper, J.M.E., Colton, R.J., and Feldman, L.C. (Eds.), No. 165, p. 122, (1987).
119. Nakajima, H., Yamaguchi, S., Iwasaki, K., Morita, H., Fujimory, H., and Fujino, Y., Applied Physics Letters, vol. 53, p. 1437, (1988).
120. Aslam, M., Soltis, R.E., Logothetis, E.M., Ager, R., Mikkor, M., Win, H., Chen, J.T., and Wenger, L.E., Applied Physics Letters, Vol. 53, p.153, (1988).
121. Stamper, A., Greve, D.W., Wong, D., and Schlesinger, T.E., Applied Physics Letters, vol. 52, p. 1746, (1988).
122. Liou, S.H., Hong, M., Kwo, J., Davidson, B.A., Chen, H.S., Makahara, S., Boone, T., and Felder, R.J., Applied Physics Letters, vol. 52, p. 1735, (1988).
123. De Vries, J.W.C., Dam, B., Heijman, M.G.J., Stollman, G.M., Gijs, M.A.M., Hagen, C.W., and Griessen, R.P., Applied Physics Letters, vol. 52, p. 1904, (1988).
124. Brown, R., Pendrick, V., Kalokitis, D., and Chai, B.H.T., Applied Physics Letters, vol. 57, p. 1351, (1990).
125. Berkowski, M., Pajaczkowska, A., Gierlowski, P., Lewandowski, S.J., Sobolewski, R., Gorshunov, B.P., Kozlov, G.V., Lyudmirsky, D.B., Sirotinsky, O.I., Saltykov, P.A., Soltner, H., Poppe, U., Buchal, Ch., and Lubig, A., Applied Physics Letters, vol. 57, p. 632, (1990).
126. Sugimoto, T., Yoshida, M., Yamaguchi, K., Sugawara, K., Shiohara, Y., and Tanaka, S., Applied Physics Letters, vol. 57, p. 928, (1990).

127. Sullivan, B.T., Osborne, N.R., Hardy, W.N., Carolan, J.F., Yang, B.X., Michael, P.J., and Parsons, R.R., *Applied Physics Letters*, vol. 52, p. 1992, (1988).
128. Eckstein, J.N., Bozovic, I., Schlom, D.G., and Harris, Jr., J.S., *Applied Physics Letters*, vol. 57, p. 1049, (1990).
129. Lee, W.Y., Lee V.Y., Salem, J., Huang, T.C., Savoy, R., Bullock, D.C., and Parkin, S.S.P., *Applied Physics Letters*, vol. 53, p. 329, (1988).
130. Hammond, R.B., Negrete, G.V., Bourne, L.C., Strother, D.D., Cardona, A.H., and Eddy, M.M., *Applied Physics Letters*, vol. 57, p. 825, (1990).
131. Jia, Q.X., and Anderson, W.A., *Applied Physics Letters*, vol. 57, p. 304, (1990).
132. Myoren, H., Nishiyama, Y., Miyamoto, N., Kai, Y., Yamanaka, Y., Osaka, Y., and Nishiyama, F., *Japanese Journal of Applied Physics Letters*, vol. 29, p. L955, (1990).
133. Matthiesen, M.M., Rubin, L.M., Williams, K.E., and Rudman, D.A., *Advances in Cryogenic Engineering Materials*, vol. 36, Reed, R.P., and Fickett, F.R., (Ed.), Plenum Press, New York, (1990).
134. Hirochi, K., Adachi, H., Setsune, K., Yamazaki, O., and Wasa, K., *Japanese Journal Applied Physics*, vol. 26, p. L1837, (1987).
135. Tanaka, S., and Itozaki, H., *Japanese Journal Applied Physics*, vol. 27, p. 622, (1988).
136. Hatta, S., Higashino, H., Hirochi, K., Adachi, H., and Wasa, K., *Applied Physics Letters*, vol. 53, p. 148, (1988).
137. Braginski, A.I., Talvacchio, J., Gavaler, J.R., Forrester, M.G., and Janocko, M.A., *SPIE vol. 948, High-Tc Superconductivity: Thin Films and Devices*, (1988).
138. Qui, X.G., Cui, C.G., Zhang, Y.Z., Li, S.L., Zhao, Y.Y., Xu, P., and Li, L., *Journal Applied Physics*, vol. 68, p. 884, (1990).
139. Itozaki, H., Higaki, K., Harada, K., Tanaka, S., Yazu, S., and Tada, K., *Physica C*, vol. 162-164, p. 367, (1989).
140. Hohler, A., Guggi, D., Neeb H., and Heiden C., *Applied Physics Letters*, vol. 54, p. 1066, (1989).
141. Wu, X.D., Inam, A., Hegde, M.S., Wilkens, B., Chang, C.C., Hwang D.M., Nazar, L., and Venkatesan, T., *Applied Physics Letters*, vol. 54, p. 754, (1989).
142. Berezin, A.B., Yuan, C.W., and de Lozanne, A.L., *Applied Physics Letters*, vol. 57, p. 90, (1990).
143. Yi, H., Wang, R., Li, H., Chen, Y., Yin, B., Ron, X., Li, L., *Applied Physics Letters*, vol. 56, p. 2231, (1990)

END

DATE FILMED

02 / 05 / 91

