A Critical Analysis of Techniques and Basic Phenomena Related to Deposition of High Temperature Superconducting Thin Films

Orlando Auciello
North Carolina State University

Alan R. Krauss
Argonne National Laboratory

Angus I. Kingon
North Carolina State University

Michael S. Ameen
North Carolina State University

Utah State University
MERRILL-CAZIER LIBRARY

A CRITICAL ANALYSIS OF TECHNIQUES AND BASIC PHENOMENA RELATED TO DEPOSITION OF HIGH TEMPERATURE SUPERCONDUCTING THIN FILMS

Orlando Auciello,*,[1,2] Alan R. Krauss,[3] Angus I. Kingon [2] and Michael S. Ameen [2]

1. Microelectronics Center of North Carolina, Research Triangle Park, NC 27709-2889
2. North Carolina State University, Department of Materials Science and Engineering, Raleigh, NC 27695-7907
3. Argonne National Laboratory, Chemistry and Materials Science Divisions, Argonne, IL 60439

Abstract

The processes involved in plasma and ion beam sputter-, electron evaporation-, and laser ablation-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. 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. Research is now demonstrating that the introduction of oxygen into the growing film, simultaneously with the deposition of the film components, is necessary to produce as-deposited superconducting films at relatively low substrate temperatures.

*Address for Correspondence:
Orlando Auciello
Microelectronics Center of North Carolina
P.O. Box 12889 (3021 Cornwallis Rd.)
Research Triangle Park, NC 27709-2889.
Telephone No. 919 248 1872
FAX No. 919 248 1455

Introduction

The discovery of the new high temperature superconducting materials (Bednorz and Muller, 1986, Wu et al., 1987a, Maeda et al., 1988, Sheng and Hermann, 1988) 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, present research indicates that thin films possess better current carrying capabilities and microstructures than their 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.

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 specifically developed techniques for thin film deposition and others adapted from more general coating technologies have been applied for synthesizing high temperature superconducting films (Harper et al. (Eds.), 1988). However, it appears that techniques based on sputtering, which involve the exposure of solid targets to plasmas or ion beams, laser ablation, or evaporation, which involve solid target exposure to high current electron beams or vaporization in effusion sources such as those used in molecular beam epitaxy deposition, are emerging as the leading methods which are both compatible with technologically feasible deposition rates and currently used techniques for device fabrication. These methods appear capable of producing the high quality, high purity, epitaxial films, necessary to optimize materials properties and performance. Other techniques have been applied for the production of high T_c superconducting films, which include, for example, chemical vapor deposition and spin-on processes. These methods, however, appear less compatible than those mentioned above with the requirements of superconducting device fabrication technology. For example, spin-on processes (May et al., 1988) produce

films with poor grain-grain contact, and must be subjected to an annealing step at $> 900\,°C$, as for $YBa_2Cu_3O_{7-x}$ for example, in order to sinter the disconnected islands of superconducting materials. 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.

Only those techniques which until now appear more compatible with device fabrication technologies will be discussed here. 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. It is impossible to cite all the literature in this rapidly growing field of research; therefore, only representative references will be cited.

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.

Review of Deposition/Processing Techniques

Plasma Sputter-Deposition

Systems and Phenomena. In plasma processing techniques (Harper et al. (Eds.), 1988), 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 filled with an inert gas to a pressure of 0.5-170 mTorr. Most studies have been performed in the 5-50 mTorr range. 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 bulk superconducting targets and nominally unheated substrates were utilized (Hong et al., 1987, Lee et al., 1987a, Makous et al., 1987). Presently, the most widely accepted reason for this plasma related effect on film formation is that films are bombarded by energetic neutralized oxygen ions, as discussed below, which results in a preferential sputtering of Ba and/or Cu from the growing films (Shah and Carcia, 1988, Rossnagel and Cuomo, 1988). The partially ionized plasma is adjacent to a solid target made out of a bulk superconductor ($YBa_2Cu_3O_{7-x}$ for example) or elemental target materials (Y, Ba, Cu or their oxides for example) symmetrically distributed in front of a substrate at either close (≤ 2 cm) or long (≥ 2 up to 10 cm) separation distance. 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 **ExB**

electron drift currents converge on the cathode surface. This concept, known as magnetron sputtering (Fig. 1) results in higher cathode (target) erosion rates than other sputtering methods (Thornton, 1988). Magnetron sputter-deposition is one of the plasma related techniques most widely used at the present time.

The plasma sputter-deposition techniques have problems, 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. For example, 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 of multicomponent targets can be severe, as shown in Fig. 2 for the example of $YBa_2Cu_3O_7$ (Auciello and Krauss, 1988c). Other problems, related to obtaining layered structures and tailoring the film composition, are discussed below.
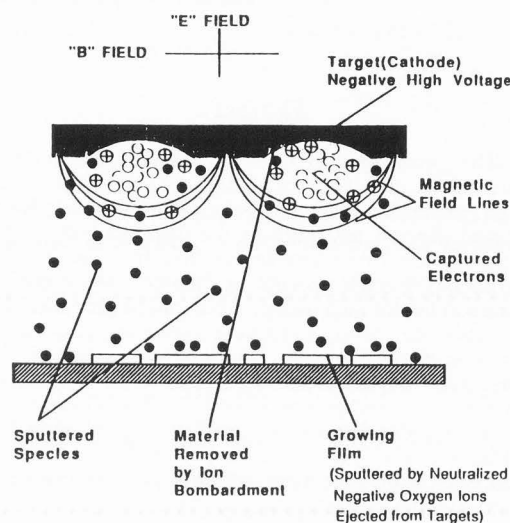

Fig.1. Cross-sectional view of a magnetron sputtering system for deposition of high T_c superconducting films.
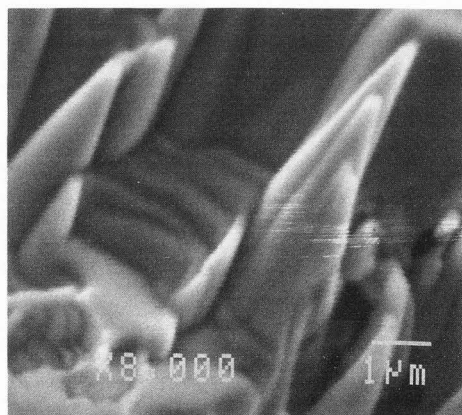

Fig. 2. SEM micrographs showing the ion bombardment-induced surface topography on an $YBa_2Cu_3O_7$ target after irradiation with an Ar^+ (10 keV) ion beam. See Fig. 8 of this review for comparison (Auciello and Krauss, 1988c).

Preferential sputtering results in compositional changes both in the lateral composition and to a certain depth below the surface of the sputtered target. 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 (Betz and Wehner, 1981).However, in most cases, a relatively thick layer must be removed before the steady-state condition is reached (Betz and Wehner, 1981), which can require bombardment of the target for as long as 10 hours (Hong et al., 1988) before the deposition starts. This extended bombardment may in turn lead to the development of substantial surface topography (Auciello and Kelly, 1984), which can also affect the sputtered fluxes of the target materials.

To overcome the problems mentioned above, some groups (Harper et al (Eds.), 1988) have used elemental materials (Y, Ba, Cu, or their oxides, Y_2O_3, BaO_2, 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. Since the targets are located in different positions, the overlapping deposition fluxes will not be identical at all points on the substrate (Kang et al., 1988a,b, and c). 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 ($\geq$ 5 inches). One method to improve compositional homogeneity with multiple sources is to increase the substrate to target distance, which 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 (Bhushan and Strauss, unpublished).

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 above, is the bombardment of the growing films by energetic neutralized oxygen ions. A relatively large number of O^- ions can be produced during the sputtering of oxide targets. These ions can be accelerated through the plasma-cathode potential fall and neutralized upon entering the plasma region. The neutralized O^- ions 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 $YBa_2Cu_3O_{7-x}$ (Rossnagel and Cuomo, 1988) and a Y_2O_3, Ba_2CO_3, and CuO multitarget arrangement (Shah and Carcia, 1988). 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. 3a) with an associated stoichiometry
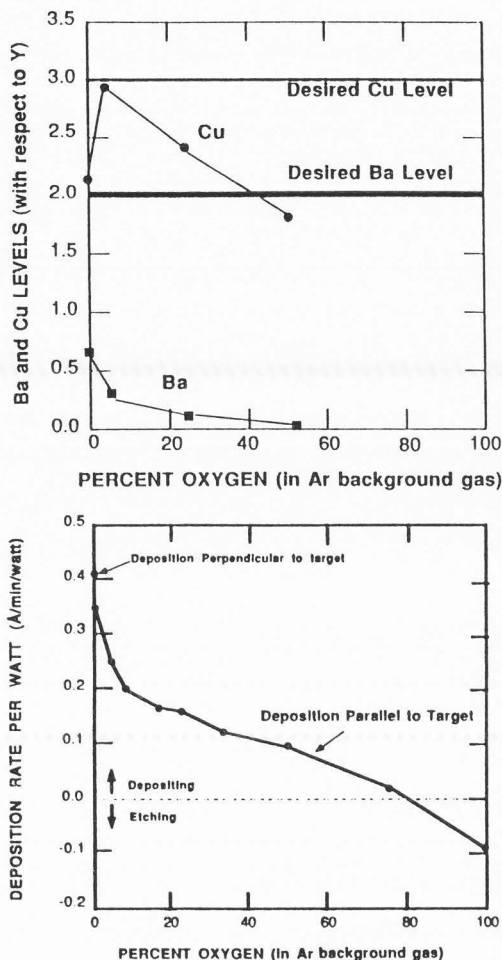

Fig. 3. (a) Net magnetron sputter-deposition rate for $YBa_2Cu_3O_{7-x}$ as a function of O_2 concentration in deposition chamber background gas. (b) Composition of a magnetron sputter-deposited Y-Ba-Cu-O film, normalized to Y=1.0, as determined by RBS (Rossnagel and Cuomo, 1988).

change (Fig. 3b); (ii) in extreme cases, the negative ion effect can actually be severe enough to produce negative growth rates; (iii) in the case of the single elemental-oxide targets 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 (Shah and Carcia, 1988); (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. 4).

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 sputter the growing film (Adachi et al., 1987). A second means of obtaining the
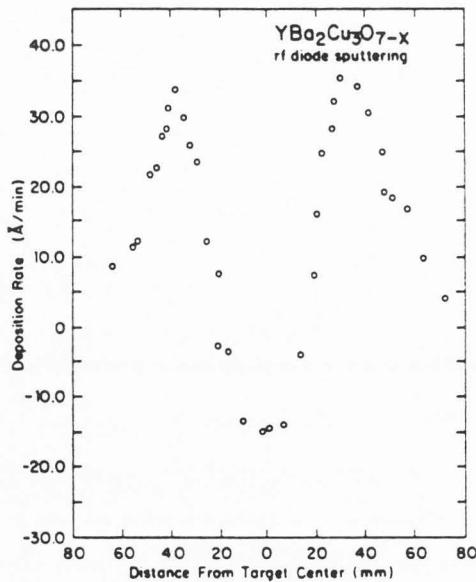
Fig. 4. Deposition/erosion rate as a function of the radial position of the substrate under the target (Shah and Carcia, 1988).
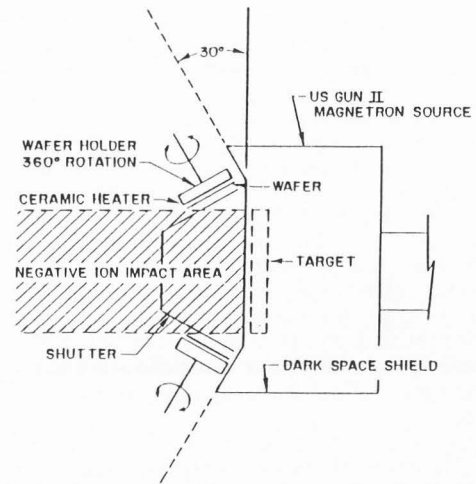

Fig. 5. Sketch of an unconventional geometrical arrangement of substrates out of the main stream of sputtered-neutralized negative ions to minimize the plasma-induced negative ion effect in plasma-assisted deposition of superconducting films (Sandstrom et al., 1988a).

The analysis of films deposited under conditions (a) and (b) yielded compositions as indicated in Table 1.

Table 1. Relationship between film compositions and deposition conditions.

Press.	Composition Deposited	
mTorr	(a)	(b)
60	$Y_{1.0}Ba_{0.68}Cu_{1.0}$	$Y_{1.0}Ba_{1.8}Cu_{3.0}$
10	$Y_{1.0}Ba_{0.30}Cu_{0.5}$	$Y_{1.0}Ba_{1.2}Cu_{0.8}$

appropriate film stoichiometry is to modify the target composition in order to compensate for the preferential sputtering associated with the negative ion effect (Moriwaki et al., 1988). This method is time-consuming and somewhat unreliable since any change in processing parameters may alter the final film stoichiometry. Unconventional sputtering geometries, in which the substrate is not subject to ion impact (Fig. 5) (Sandstrom et al., 1988a), 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. (1988) 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.

The analysis of the four sketches in Fig. 6 indicates the following: (a) Both secondary neutralized ions and electrons impact on 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, see text). (d) Bombardment of both secondary electrons and ions is eliminated. Again, it is not clear from the discussion presented by Terada et al. (1988) what is the main difference between (c) and (d).

Terada et al. (1988) argued that the data presented in Table 1 demonstrates that the suppression of electron bombardment in condition (b) resulted in films which are closer to stoichiometric compositions. However, a careful analysis of the film composition as a function of gas pressure in Table 1 indicates that the transverse magnetic field may not be the only factor contributing to minimizing the secondary electron bombardment of the growing film, but also that the gas pressure may play a relevant role in slowing down these electrons by collisions with plasma species (mainly ions and neutral atoms). In fact, recent work performed by Auciello et al (1990a) indicates that the intensity of the secondary electrons emitted from $YBa_2Cu_3O_{7-x}$ targets exposed to Ar plasmas is significantly reduced as a function of gas pressure and distance from the target. 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) (Auciello et al., 1990a).

In any case, film compositional changes 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
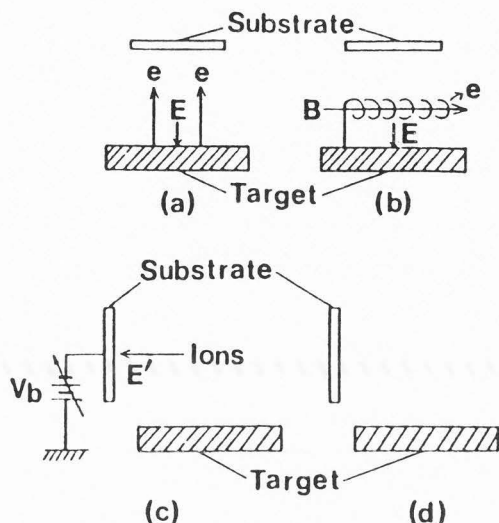
Fig 6. Methods for minimization or elimination of secondary electron and ion bombardment of growing high T_c superconducting films in plasma sputter-deposition (Terada et al., 1988).

bombardment may not be a major contributor to film stoichiometry alteration, which may be due mainly to energetic neutralized oxygen ion bombardment, a dominant phenomenon in both types of plasma-sputtering systems, or if not proper sputter-conditioning of the target is performed, also due to preferential sputtering of the target.

More recently, Klein and Yen (1990) performed systematic experiments to study the influence of r.f. sputter variables on the composition of $YBa_2Cu_3O_{7-x}$ films. These studies involved measurements of composition and thickness of Y-Ba-Cu-O films synthesized by r.f. plasma sputter-deposition as a function of chamber pressure, r.f. power, and substrate position. The main results, which partially confirmed some of the effects discussed above, were:

(i) A slight increase in Cu and Y, and a decrease in Ba content of the films for a pressure increase between 3 and 20 mTorr.

(ii) A noticeable dependence of deposition rate on pressure, such that a significantly higher rate was observed at 6 mTorr, this probably due to a competition between ion collection by the cathode and gas scattering of the sputtered material.

(iii) A slight increase in Y and Ba, and a decrease in Cu content of the films as a function of increasing power in the range of 20 to 75 watts.

(iv) A rapid increase in deposition rate for increasing power in the same range as above.

(v) A rapid increase in Cu and decrease in Ba film content, concurrent with a slight increase in Y as a function of increasing target-substrate distance in the range 30 to 50 mm. This may be explained in terms of collisional slowing processes during the transport of sputtered species through the plasma, as suggested by measurements of this effect by Auciello et al. (1990a).

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.

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 $YBa_2Cu_3O_7$ bulk superconductors were used as targets, but frequently resulted in deficiencies of Cu (Adachi et al., 1987, Bullock et al., 1987, Michikami et al., 1987, Ohkuma et al., 1987) or Ba (Lee et al., 1987a, Shah and Carcia, 1988, Rossnagel and Cuomo, 1988, Han et al., 1987, Bullock et al., 1987) 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 (Michikami et al., 1987), 1:2:4.5 (Enamoto et al., 1987, Adachi et al., 1987, Kamada et al., 1988), 1:2:9 (Ohkuma et al., 1987, Mochiku et al., 1988), 1:4.4:3. (Han et al., 1987), 1:3.2:3.9 (Bullock et al., 1987), 1:3.4:4.6 (Bruyere et al.,1988), 1:3:7 (Onuma et al., 1988), 1:4:7 (Hu et al., 1988), 1:3:6 or 1:2.5:4.5 (Gawalek et al., 1988) have been used.

An alternative method for stoichiometry adjustment in the film involves the co-sputtering of both a stoichiometric and a Ba or Cu target simultaneously exposed to the plasma. Both metallic and oxide targets have been used in different experiments (Michikami et al., 1987, Lanchbery, 1988, Aida et al., 1989).

Other groups have used either all three metallic (Ginley et al., 1988, Blamire et al., 1987, Gurvitch and Fiory, 1987, Silver et al., 1987) or combinations of metallic and binary alloy targets such as Ba_2Cu_3/Y (Gurvitch et al., 1987, Makous et al., 1987), $YCu/BaCu/YCu_3/Ba$, sputtered in a 1:2 ratio (Scheuermann et al., 1987), and $Y/Cu/Ba_2CuO_3$ in a multitarget magnetron sputtering system (Miura et al., 1988a).

In all plasma sputter-depositions where metallic targets have been used, oxygen was present in the plasma, which resulted in partially oxidized films. This partial oxidation was, however, not enough to prevent the material degradation upon exposure to atmospheric pressure, which is particularly critical for $YBa_2Cu_3O_7$. Here, it is relevant to make a comparison between the plasma and ion beam sputter-deposition methods. In the latter, the deposition, simultaneously with a dynamic oxidation of the growing layers, yield films, which do not appear to degrade upon atmospheric exposure any more than similar films produced by sputtering of oxide targets would degrade. 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 (Makous et al., 1987), or by immediate post-deposition *in situ* or *ex situ* oxidation of the YBaCu metal films (Makous et al., 1987). 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 methods discussed above to control film stoichiometry are highly empirical, and their potential to yield reproducible high quality films with excellent superconducting characteristics are questionable.

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

Substrate temperatures used span the range from room temperature to 900 °C. Films deposited at < 500 °C were generally amorphous as-deposited, but not necessarily after annealing, while the orthorhombic 123 phase characteristic of superconducting Y-Ba-Cu-O films or Y-substituted compounds such as Er-Ba-Cu-O were obtained at

substrate temperatures in the range 650 -800 °C (Adachi et al., 1987, Mochiku et al., 1988). In all cases, 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 (Lin et al., 1988) or 560 °C (Miura et al., 1988a). However, neither the accuracy of the temperature measurements nor the exact plasma conditions under which those films were produced have been clearly established. A point to be considered is that oxygen pressure in the plasma in conjunction with the substrate temperature may act synergistically to control the film composition and crystallinity. For example, Li et al. (1988) reported that Y-Ba-Cu-O films produced at 0.2 Torr of oxygen partial pressure and substrate temperature of 770 °C presented the oxygen "deficient" tetragonal form, which was transformed into the orthorhombic one upon heat treatment at 430 °C in an oxygen atmosphere. From an analysis of various experiments presented in the literature, 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 film stoichiometry.

Film composition appears to be also sensitive to the combined effect of both target-substrate distance and gas pressure. This is particularly applicable to plasma sputter-deposition. For example, a distance > 4 cm resulted in Ba deficient and Cu rich films, in plasma sputter-deposition involving multicomponent superconducting oxide targets. Conversely, Cu deficient films were produced in experiments where metal targets were used such that the target-substrate distance was > 10 cm. Adachi et al. (1987) found, for example, that superconducting films were produced when the target-substrate distance was about 2-3.5 cm, while the tetragonal semiconducting phase was obtained for distances in the range 4-6 cm. The range of distances that can be employed may also depend on whether the plasma system operates in the r.f. or d.c. mode. Recent studies on the transport, throughout a d.c. plasma, of species (Y, Ba, Cu) sputtered from $YBa_2Cu_3O_7$ targets, revealed that collisions between the sputtered species and inert gas atoms in the plasma results in a mixture of slowing down, backscattering, and diffusion processes. These can affect the displacement and therefore the distance travelled by the sputtered particles in the plasma. Additionally, through the combination of target-substrate distance/gas pressure, the composition of the films can also be affected (Auciello et al., 1990a).

The Y/Ba/Cu ratio needed to achieve a superconducting transition is not necessarily 1:2:3, but the closer to that ideal ratio the higher is 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 (Bullock et al., 1987). This was explained by considering that the non-stoichiometric material still had the superconducting orthorhombic structure after an appropriate annealing (Bullock et al., 1987). However, other researchers (Wiesmann et al., 1989) 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 (Eom et al., 1989, Klein et al., 1990). This corresponds to a region of cation solid solution, viz incorporation of additional CuO_2 planes,

and is unlike the behavior of sintered ceramic $YBa_2Cu_3O_{7-x}$ specimens. Obviously, further work is warranted to clarify the interdependence of composition vs. crystallographic structure that result in superconducting films.

Considerable spatial inhomogenity has been observed in the sputtering flux of a plasma environment. This can result in compositional variations across the film surface, as previously shown in Fig. 4. This effect is particularly pronounced in plasma systems involving a parallel plate geometry. It has been determined, 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 different collisional slowing down processes in the plasma for species with different masses, as discussed above, which can also affect the sputtered flux distribution for different species. These effects may be important according to preliminary studies recently conducted by Auciello et al. (1990a). Both the thickness profile and concentration variations were radially symmetric (Burbidge et al., 1987, Lanchbery, 1988).

Uneven angular distribution in the sputtering yield of the constituents of multicomponent materials may be a problem with planar targets (Whener et al., 1988), particularly for high ion bombardment doses that produce strong topographical changes on the target surface (Auciello and Kelly (Eds.), 1984), which partially contribute to these variations through geometric effects (Bullock et al., 1987). Wehner et al. (1988) suggested a unique method for reducing the geometric effects introduced by the planar target geometry. They used a spherical target (Fig. 7) exposed to a Hg plasma. Advantages that Whener et al. (1988) 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; this statement is, however, based on empirical considerations, and further work with this geometry is necessary to confirm this ascertion.

(b) the use of a relatively low ionization potential gas, such as Hg, which allows formation of a plasma with a low voltage that reduces the acceleration of the negative particles emitted from the oxide targets (O^- ions and secondary electrons, as discussed above), and therefore 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.

Deposition rate may also affect the quality of the 123 films. Akune and Sakamoto (1988) observed, for example, sharp superconducting transitions in films deposited at low rates, while others deposited at higher rates showed broad transitions.

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.

Thermal Evaporation Techniques

The term thermal evaporation is used to designate those methods that involve the evaporation of material in thermodynamic equilibrium from solid targets. The main techniques are electron beam or resistive heat-induced evaporation and molecular beam epitaxy (MBE). Here, it is relevant to clarify the terminology that is used. Originally, MBE was utilized to designate the method whereby epitaxial films are deposited on a single by single layer basis. Distinctive features of this technique, as initially
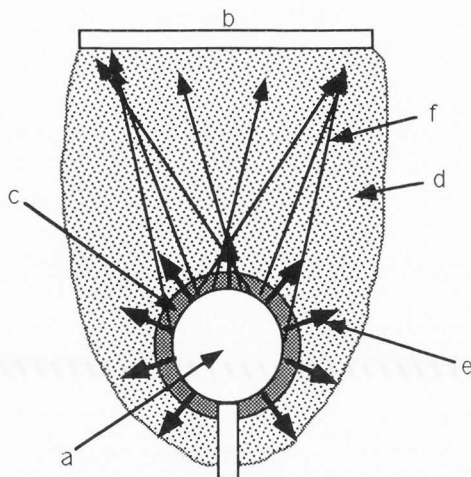
Fig. 7. Sketch showing a plasma sputter-deposition system with spherical target/planar substrate geometry. The radius of the sphere is 5 mm and the target-substrate distance 15 mm for this particular system. (a) Is the spherical target, (b) is the substrate, (c) is the plasma sheath, (d) is the Hg plasma, (e) represents the negative oxygen ions, and (f) are the sputtered species (Wehner et al., 1988).

Fig. 8. Sketch of an electron beam vapor-deposition system for production of high T_c superconducting films.

implemented, were: (a) the effusion cells, where materials were evaporated by resistive heating, and (b) the accurate thermodynamic and geometrical control of the vapor flux required to produce monolayer by monolayer deposition. More recently, however, several groups have successfully used electron beams to produce controlled evaporation of particular elemental materials (constituents of superconducting films), in hybrid systems, where the other film components were evaporated in effusion cells, such that a monolayer by monolayer deposition was achieved. Based on the discussion presented above, the main difference between the simply called electron beam and/or resistive evaporation and the molecular beam epitaxy (MBE) techniques is the capability for the latter of producing monolayer by monolayer deposition, and both will be discussed in this context in the following sections.

Electron Beam and Resistive Evaporation. These two methods present similarities and therefore are described jointly here. Elemental materials (e.g., Y, Ba, Cu) are co- or sequentially deposited on appropriate substrates. Sequential evaporation appears to provide better control of film stoichiometry (Tsaur et al., 1987). Recently, "flash evaporation" (Hatou et al., 1988), "reactive evaporation" (Terashima et al., 1988), and "plasma enhanced evaporative deposition", where oxygen is dynamically introduced into the growing films by a remote plasma source (Moriwaki et al., 1988), have also been demonstrated.

The electron beam evaporation technique, as hitherto implemented (Laibowitz et al., 1987, Hammond et al., 1987, Harper et al. (Eds.), 1988) has mainly involved the use of individual thermionically produced electron beams, with energies in the range of 5 to 10 keV, magnetically deflected, and focused onto spatially separated elemental metallic (Y, Ba, Cu for example) or alloy targets (Chaudhari et al., 1987a, Laibowitz et al., 1987, Oh et al., 1987, Tsaur et al., 1987, Mogro-Campero et al., 1988, Terashima et al., 1988) located in water-cooled holders (Fig. 8).

An alternative approach used by some groups has been to evaporate Y and Cu with an electron beam, while Ba was evaporated in an effusion cell (Schellingerhout et al., 1988).
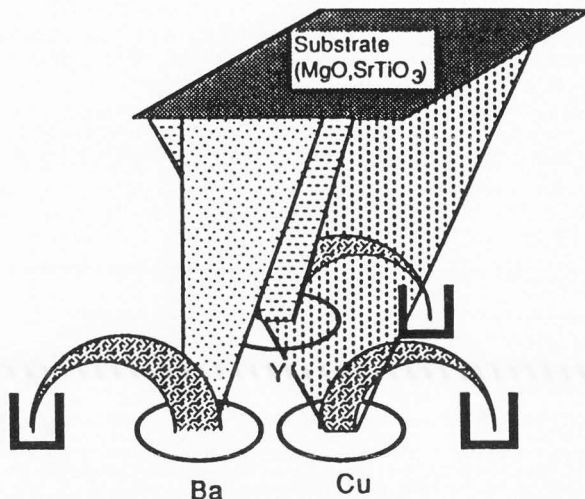
A problem related to the use of Ba metal is the rapid oxidation of this material (the surface turns rapidly into a white powder containing barium oxide and carbonate) when exposed to air, which complicates target preparation and surface state preservation prior to introducing the target into the deposition chamber. For this reason, a common practice has been to use inert compounds, such as BaF_2, $BaCO_3$, BaO, BaO_2 (Bao et al., 1987, Fisanick et al., 1987, Mogro-Campero and Turner, 1988, Qiu and Shih, 1988, Sorimachi et al., 1987). For similar reasons, yttrium oxide has also been used as a source of yttrium (Bao et al., 1987, Sorimachi et al., 1987). In principle, it would be desirable not to use compounds that may result in the incorporation of undesirable elements into the films. However, it is interesting to note that films produced using BaF_2 contained only a small amount of F ($< 5\%$), which apparently did not affect their superconducting characteristics (Hatou et al., 1988).

The deposition of metals has usually been done by putting sets of trilayers (Y, Ba, Cu, for example, in different sequences), with the layer thicknesses adjusted to provide the desired 123 stoichiometry. The number and order of the layers have varied for different experiments, although Cu has been used in many instances as the first layer in contact with the substrate because it has the lowest oxygen affinity, which may minimize film/substrate interactions (Tsaur et al., 1987). However, the sequence Ba, Y, Cu has also been utilized (Qiu and Shih, 1988).

There are some specific problems related to vapor-deposition that have to be considered. The preparation of $YBa_2Cu_3O_7$ films by metal deposition and oxidation appears to be more difficult than for the deposition of other rare earth metals, mainly because of the positive heat of mixing between Y and Ba; yttrium barium oxide tends to form preferentially instead of the 123 phase (Nastasi et al., 1987).

Another serious problem with electron beam evaporation relates to geometrical effects on the film thickness and composition. Naito et al. (1987), for example, deposited Y-Ba-Cu-O films on ten substrates positioned in a row facing three linearly spaced Y, Ba, and Cu electron beam evaporation sources. This geometry effectively varied the source to substrate distance and the angle of incidence for each of the components. The stoichiometry of the films

changed in the range 1:1.35:2.65 to 1:2.79:3.36 for Y, Ba, and Cu respectively. This effect may be reduced by locating the sources on a circle and distributing the substrates on a circular area centered with respect to the sources. However, geometric problems may still be above desirable limits.

Deposition of Y-Ba-Cu-O films by evaporation of $YBa_2Cu_3O_7$ targets has also been explored. A major problem was that the targets thermally decomposed into the original oxides (CuO, BaO, and Y_2O_3), used to make the pellets, which have different vapor pressures. CuO evaporated first followed by BaO and Y_2O_3. This resulted in Y deficient films and an extra Y layer was necessary to achieve the 123 stoichiometry (Terasaki et al., 1988).

The role of the substrate temperature on vapor-deposited superconducting films is still unclear. The most widely used substrate temperature range, during deposition, has been 300-500 °C. This temperature, however, was optimum for the initial work, which involved post-deposition annealing. Laibowitz et al. (1987) indicated, for example, that film stability is increased when deposited at intermediate temperatures (450 °C). On the other hand, Naito et al. (1987) suggested that the substrate temperature, during deposition, does not significantly affect the T_c, but it influences the J_c and the shape of the R vs. T curve. However, the reports on this particular subject are contradictory. Naito et al. (1987) measured high J_c values in films deposited at at ambient temperature on $SrTiO_3$, while they were lower for deposition at higher temperatures (700-900 °C). The proposed explanation for this behavior (Naito et al., 1987) was that random orientation was dominant in films deposited at high temperatures, while for deposition at 300-500 °C the films had their **a**-axes oriented perpendicularly to the substrate surface. At lower temperatures, the orientation appear to be even stronger, with the **c** axis perpendicular to the substrate. Contrary to Naito et al. (1987) results, Tietz et al. (1988) succeeded in depositing films with high T_c at 700 °C. Obviously, further work is necessary to clarify the contradictory results discussed above.

Generally, in the usual implementation of the electron beam evaporation method, process parameters, particularly precise film stoichiometry and abrupt interfaces, are difficult to reproduce and control, since direct shuttering of individual beams near each source is difficult without disturbing the focused magnetic flux and thus quenching the evaporation of the target material. The simultaneous evaporation of the elemental materials from different spatial locations tends to produce non-uniformity in composition and thickness across the film surface. This presents a similar problem as that previously discussed for plasma-assisted deposition for covering large areas with uniform films. The film nonuniformity and the shuttering problem have been partially overcome by placing the substrate on a moveable holder. The substrates are sequentially positioned over each hearth for a pre-determined time to produce the desired layer thicknesses. For deposition of $YBa_2Cu_3O_{7-x}$ thin films, if the layer thicknesses are of the order of 50 Å, the subsequent annealing step suffices to produce a completely homogeneous film.

It should be noted that whatever geometrical arrangements described above is used, the need for one electron gun for each target adds complexity and cost to the hardware, because of the necessary replication of the electronics required to control each source. Accurate adjustment of the sources to keep the evaporation rate of each material within tight tolerances is mandatory in order to produce stoichiometric films. This problem is obviously

accentuated as the number of elemental material components of the films increases.

Little can be discussed about basic phenomena involved in electron beam-induced evaporation, as studies on transport processes of evaporated species and film characteristics dependence on geometrical arrangements have not been performed according to the authors' present knowledge. Evaporation with simultaneous supply of active oxygen (or "activated reactive evaporation" - ARE) is extremely important for controlling the crystallinity and oxygen content of the films in order to produce as-deposited superconducting films at low substrate temperature. These processes are discussed below in further detail.

Molecular Beam Epitaxy (MBE). This technique has not been used as extensively as the others discussed in this review. The method has been mainly applied to synthesizing $YBa_2Cu_3O_7$. Films with 123 stoichiometry have been produced by using metals as source materials (Kwo et al., 1987, Kwo et al., 1988, Webb et al., 1987, Schlom et al., 1988, Liou et al., 1987). Generally, the three metals were simultaneously deposited by concentrating the vapor fluxes of three MBE sources onto a substrate centrally located with respect to the sources symmetrically distributed on a circular area. An electron beam heater was used to evaporate the rare earth, while Ba and Cu were vaporized in effusion cells. Each element deposition rate was first individually monitored and subsequently adjusted to yield the desired 123 stoichiometry. Different deposition schemes were explored, such as continuously deposited Cu with periodically shuttered Dy and Ba fluxes to create a layered structure (Schlom et al., 1988) or uninterrupted deposition of the three elements (Kwo et al., 1988).

The deposition conditions, in the references cited above, generally included:

(a) Base pressures in the range of 10^{-10} Torr or less, which increased to the 10^{-7} Torr range upon oxygen introduction into the deposition chamber, previously to initiating the film synthesis. The pressure during the film growth was commonly in the range of 10^{-5} Torr.

(b) Substrate temperatures in the range 450-750 °C.

(c) Different substrates, which can be classified in increasing order of success, for yielding high quality films, as Si (100), sapphire (100), Y stabilized ZrO_2 (100), MgO (211), and $SrTiO_3$ (100) and (110).

MBE, as the techniques previously discussed, also presents the scaling-up problem related to covering large areas with films uniform in thickness and composition. Therefore, future work should involve efforts directed at solving this problem.

Film characteristics and qualities are discussed below, in a separate section including a comparative analysis of the film properties obtained by the different techniques described in this review.

Laser Ablation Deposition

Pulsed lasers have been used to deposit Y-Ba-Cu-O films by ablation of sintered $YBa_2Cu_3O_7$ targets (Dijkkamp et al., 1987, Narayan et al., 1987, Harper et al. (Eds.), 1988). This appears, currently, to be one of the more successful techniques used for producing high T_c films from bulk superconductor targets on a laboratory scale. However, some characteristics of the laser ablation process, determined in recent studies, indicate that laser ablation-deposition, as hitherto implemented, may present some difficult problems, particularly those related to controlling films characteristics over large areas for scaled-up industrial applications . Some of these problems are discussed below.

The hardware initially used by different groups to

produce high T_c superconducting films involved an ultra-high vacuum deposition chamber, containing a rotatable target holder, a substrate heater, and a laser system (Dijkkamp et al., 1987, Narayan et al., 1987, Harper et al. (Eds.), 1988, Margaritondo et al. (Eds.), 1989). Lasers that have been used by different groups include : pulsed, ArF (193 nm) (Kwok et al., 1988, Kawai et al., 1988), KrF (248 nm) (Dijkkamp et al., 1987, Barton et al., 1987, Mashburn et al., 1988, DeSantolo et al., 1988), XeCl (308 nm) (Narayan et al., 1987), CO_2 (10.6 µm) (Barton et al., 1987), transversely excited atmospheric pressure CO_2 (Miura et al.,1988b), Nd:YAG (1.064 µm) (Lynds et al., 1987a, Eryu et al., 1988), CW Nd:YAG (Kwok et al., 1988), and Q-switched Nd:YAG (532 nm) (Komuro et al., 1988) lasers. Laser parameters that have been used include: (a) laser energies of about 100 J/pulse, (b) energy densities in the range of 0.5-3 J/cm^2, (c) frequencies in the range 3-300 Hz, and (d) pulse widths that varied from nanosecond to millisecond.

More recently, various groups added diagnostics instrumentation to study the plasma generated by the laser upon impact on the target. Optical emission (Auciello et al., 1988a, Weimer, 1988, Ying et al., 1988) and absorption (Geohegan and Mashburn, 1989) spectroscopies, and mass spectrometry (Dijkkamp et al., 1987, Lynds et al., 1987b, Kawai et al., 1988) have been used to determine the predominant species in the laser-induced plasma plume. A typical geometry for a laser ablation-deposition system, including the diagnostics mentioned above, is shown in Fig. 9. The system depicted in that figure, however, includes some special hardware, which is part of a new concept for automated laser ablation-deposition of high T_c films, developed by Auciello and Krauss (unpublished, 1989). Until recently, all laser ablation-deposition experiments involved the use of multicomponent-oxide superconductor targets. The new deposition concept by Auciello and Krauss (unpublished, 1989) involves a computer-controlled system that features a rotatable target holder, where elemental materials (Y, Ba, Cu, for example) or their simple oxides (Y_2O_3, BaO, CuO) are sequentially exposed to an excimer laser. A quartz crystal resonator (QCR) is used to measure the amount of each element deposited on the substrate, and a feedback signal is sent to the computer when the required amount of each element necessary to achieve the desired film composition has been deposited. The signal is used to turn the laser off and rotate the holder to expose a new target to the laser. The main objective in developing such a deposition system was to overcome some of the problems related to the laser ablation-deposition technique, which are described below.

Problems related to the laser ablation-deposition technique are considered below in the context of a discussion of some basic laser-target interaction and ablated plume transport phenomena.

For multi-oxide superconductor targets, the target stoichiometry is not exactly reproduced in the deposited films, a fact which may contribute to the observed slightly lower T_c in these films. Dijkkamp et al. (1987), Auciello et al. (1988b) and Sudarsan et. al. (1988) have shown that the variation in film composition may be due, at least partially, to significant topographical and associated compositional changes on the target surface induced by the laser impact during the ablation process (Fig. 10 for example).

Depending on the laser power and wavelength (Auciello et. al.,1988b), Sudarsan et al., 1988), extreme variations in target composition and morphology have been observed at various points in the laser-induced etch pit. For a XeCl (308 nm, ~ 3 J/cm^2) excimer laser irradiation of
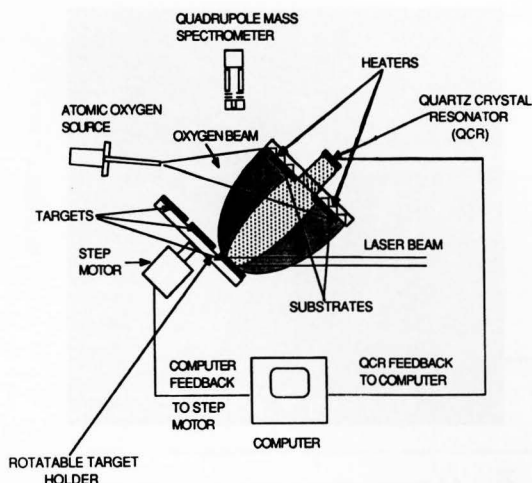

Fig. 9. Schematic of a laser ablation-deposition system, including optical spectroscopy and mass spectrometry instrumentations. The particular system shown in this figure contains special hardware pertaining to a new laser ablation-deposition concept developed by Auciello and Krauss (unpublished, 1989) (see text).

$YBa_2Cu_3O_7$, Auciello et al. (1988b) found a Cu depletion at the center of the laser impacted area, while Sudarsan et al. found Cu enrichment at a similar position, when irradiating also a 123 target with an ArF (193 nm, 0.41 J/cm^2) excimer laser. These results indicate that more systematic studies are necessary to elucidate the effect that the irradiation of superconductor targets, by lasers of different wavelength and energies, may have on the characteristics of deposited films. Laser irradiation may result in the formation of cones, as seen in Fig.8a. The presence of these features may affect surface compositional analyses in that variations in composition, from the top to the side of the cones, have recently been observed (Auciello, unpublished, 1989).

Noticeable lateral non-uniform composition and thickness of laser-vapor deposited films and angular variation in the stoichiometry of the flux of ablated species from superconductor targets has recently been observed by Singh et al. (1988), Venkatesan et al. (1988a), and Auciello (unpublished, 1989) (See Figs. 11 and 12).

Figs. 11 and 12 show that there are two distinct regions in the deposited films with different thicknesses and composition, which may be correlated with two regions in the angular distribution of the ablated species flux, i.e., a narrowly and a widely dispersed component, respectively, around the surface target normal (Venkatesan et al., 1988b). Fig. 11b indicates that the film composition in the outer region of the film, which correspond to deposition from the widely dispersed ablated flux component (attributed to thermal vaporization), does not correspond to the stoichiometric composition of the target. On the other hand, the forward-peaked component of the ablated flux appears to yield a film composition closer to that of the target.

Venkatesan et al. (1988b) have considered various possible models, briefly described in this paragraph, to explain their experimental data, which mainly relates to ablation processes produced by a KrF (248 nm) excimer laser with power densities in the range 1.5-3.5 x 10^7 W/cm^2. Within a few nanoseconds of laser impact on the target surface, material can rapidly evaporate, which may result in a subsequent forward ejection of that material due to a secondary process. The possible secondary processes that
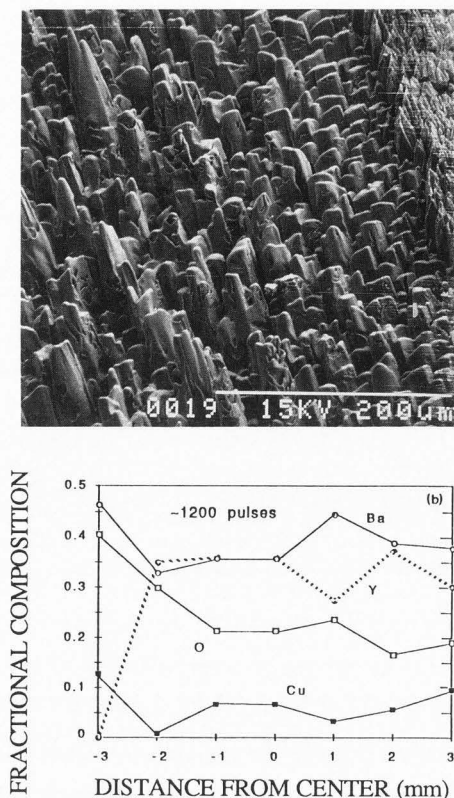
Fig. 10. (a) SEM micrographs showing a characteristic laser-induced surface topography of a single phase $YBa_2Cu_3O_7$ target impacted by 1200 pulses of an XeCl (308 nm, 0.28 J) excimer laser, during the deposition of an Y-Ba-Cu-O film. (b) AES line scans at different positions across the laser impacted surface of the same target as in (a) (Auciello et al., 1988b).
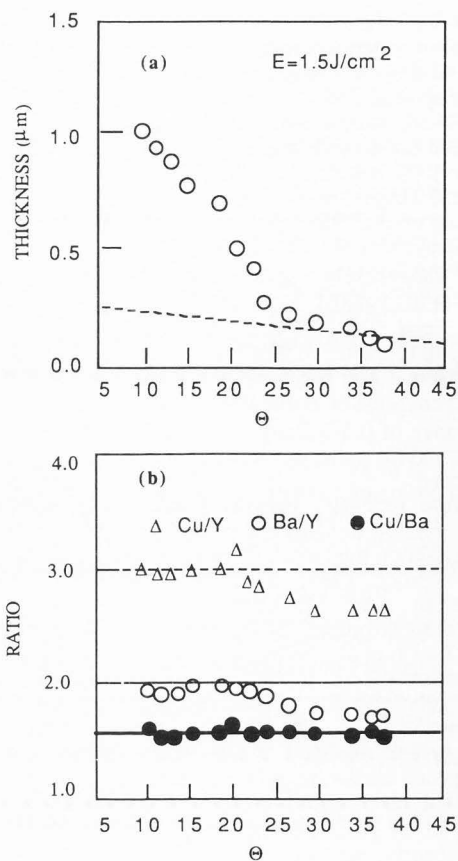

Fig. 11. Angular distributions of (a) thickness (the dashed line is the cos Θ fit) and (b) composition of an Y-Ba-Cu-O film deposited by laser ablation of an $YBa_2Cu_3O_{7-x}$ with a laser energy density of 1.5 J/cm^2 (Venkatesan et al., 1988b).

were considered are: (1) surface shock waves generated by the rapid surface evaporation, as seen in a number of laser-surface interaction studies (Bonch-Bruevich and Imas, 1968), (2) a subsurface explosion generated by a combination of a hot subsurface region, capable of building-up a high vapor pressure zone, and a cooler surface produced by the rapid evaporation of material from the surface (Gagliano and Paek, 1974), (3) the production of a high density region of ablated material in front of the laser-impacted surface (the so called Knudsen layer) (Kelly and Dreyfus, 1988), which could lead to a high number of collisions among the ablated species resulting in a recondensation process and particles emitted in a forward peaked direction.

With the data presently available, it is difficult to decide which of the mechanisms described above or their combination may be the most appropriate to describe the experimental observations, or if they generally apply to lasers of different wavelength and power.

The precise mechanisms involved in the effects discussed above are still being investigated, mainly because their understanding may be fundamental to solving possibly difficult problems. The effects described above may pose problems for scaling the laser-vapor deposition technique to the coverage of large areas, which is necessary for the integration of high T_c superconducting films with current semiconductor technology. Film thickness uniformity over

large areas could be achieved by planar motion of the substrate. However, although substrate motion may result in spatially averaged stoichiometry of the film, it may still be difficult to produce sufficient averaging of the very sharply peaked ablated flux component. Whether this problem can be solved by using a large diameter ($\geq$ 3 inches) laser beam also remains in doubt. Obviously, further work is necessary to optimize the laser ablation-deposition technique for large scale technological applications of high T_c superconducting films.

In addition to the study of the basic phenomena discussed above, an accurate understanding of the evolution of the ablated plume from the target and the transport of the ablated species towards the substrate is necessary to optimize the deposition process, and thus the film characteristics. Recently, studies have been performed on the evolution of the plasma plume generated when laser beams impact upon bulk superconductor targets. In particular, the velocity (energy) distributions of ablated species (Y, Ba, Cu, and oxide molecules (e.g. BaO)) from $YBa_2Cu_3O_{7-x}$ targets have been measured by different groups (Venkatesan et al., 1988b), Zheng et al., 1989a). The mean kinetic energies measured for Cu I (41 eV), Y I(43 eV), Ba I(42 eV), and Ba II(86 eV) are relatively high (Zheng et al., 1989a)and can in principle be explained in terms of the theory of supersonic molecular beams (Anderson et al., 1966), where the velocity
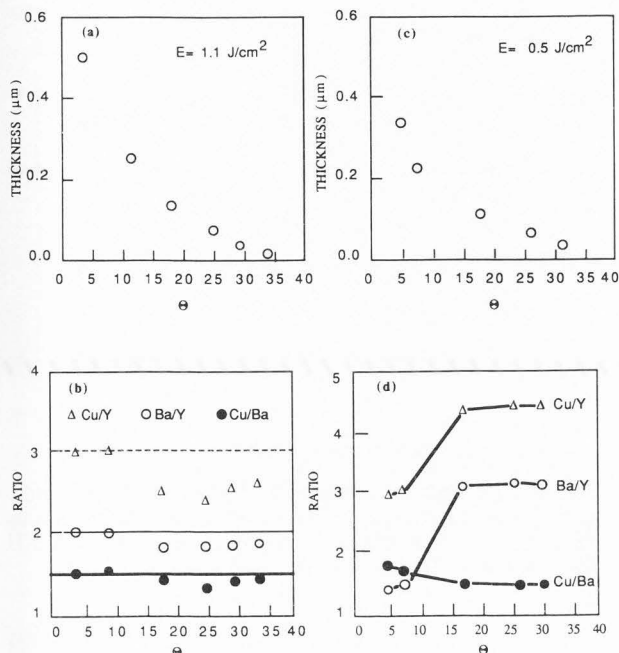
Fig. 12. Stoichiometry and thickness of Y-Ba-Cu-O films as a function of laser energy density: (a) and (b) 1.1 J/cm^2; (c)and (d) 0.5 J/cm^2 (Venkatesan et al., 1988b).

distribution function of laser ablated atoms from a solid can be expressed as:

$$f(v) = Av^3 \exp[- m(v-v_0)^2 / 2 k Ts] ,\qquad (1)$$

where v is the velocity of the atoms, v_0 is the "stream" velocity, m is the mass of the atoms, k is Boltzman's constant, T_s is a temperature parameter describing the velocity spread, and A is a normalization constant. Fig. 13 shows, as an example, typical optical emission time of flight (TOF) experimental spectra for Cu, Y, and Ba atoms ablated from an YBa$_2$ Cu$_3$O$_{7-x}$ target , by an ArF laser (193 nm), and the fitted curves obtained from eq.(1) (Zheng et al.,1989a). Additionally, measurements of ablated neutral atom velocities as a function of distance along the normal to the target surface indicated that Cu atoms appear to initially move faster than Y, Ba, and O atoms, and the velocities of all these species tend to equilibrate at about 7 cm from the target surface (Fig. 14, Zheng et al., 1989a). The almost zero velocity of the Ba II species was not explicitly discussed by Zheng et al.(1989a). However, a possible explanation proposed by the authors of this review relates to the fact that Ba II represents Ba ions in excited state. The ablated species in an ionized state are moving against an electric field established between a positively biased ring and the grounded target (Zheng et al., 1989a,b), which could effectively reduce the velocity of the Ba ions to very low values. The equilibration of the neutral atom velocities at about 7 cm from the target surface has been correlated with the experimental observation that the best quality films were obtained when positioning the substrates at that particular distance (Zheng et al., 1989a).

On the other hand, Venkatesan et al. (1988a) used laser ionization mass spectrometry (LIMS) to identify ionic species emitted from YBa$_2$Cu$_3$O$_{7-x}$ targets impacted by a Nd:YAG laser (266 nm, 5 ns pulses), and post-ablation
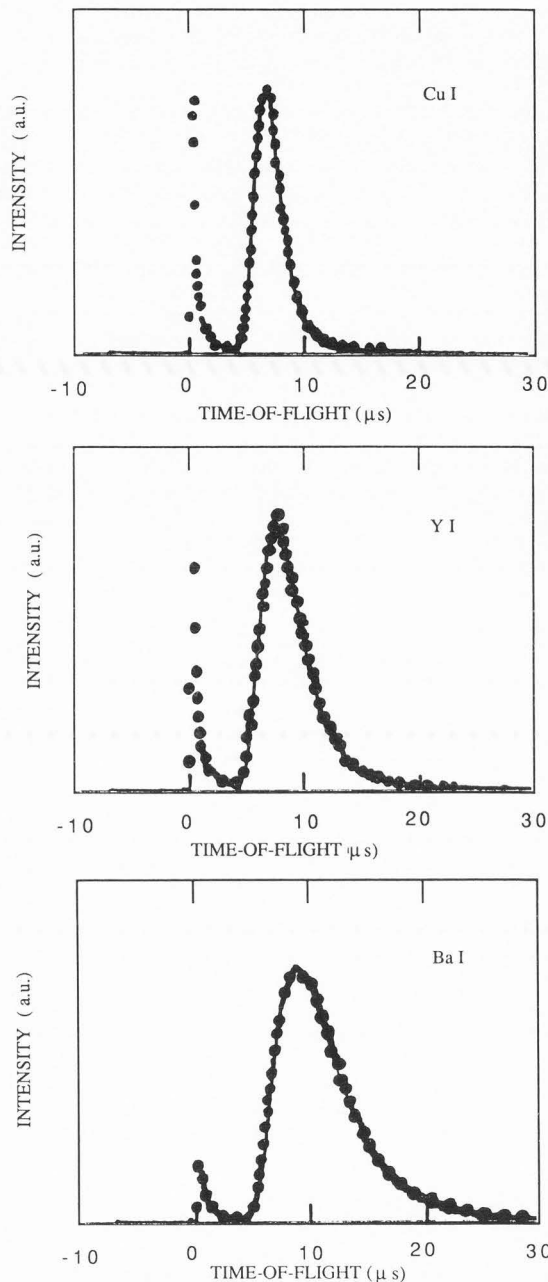

Fig. 13. Optical emission TOF spectra of Cu I, Y I, and Ba I taken at 7.2 cm from the target surface. The solid lines are theoretical fits using eq. (1), while the black dots represent experimental data. The initial spike is due to scattering and laser-induced fluorescence, and can be used as a time marker (Zheng et al., 1989a).

ionization (PAI) to determine the masses and velocities of the ablated species, which were also demonstrated to be very energetic. Both the LIMS and PAI studies indicated, according to the authors, that ejection of stoichiometric clusters of YBa$_2$Cu$_3$O$_{7-x}$ from the targets can be ruled out. Instead, binary and ternary sub-oxides were emitted from the targets, at least under the laser irradiation conditions used by Venkatesan et al. (1988a). Different laser wavelengths,

coherence, fluence, photon rates, energy, duty cycles, target and vacuum conditions, etc. may render comparisons of data obtained in separate systems unreliable. Deshmukh et al. (1988) observed mainly metallic species (Bi, Sr, Ca, Cu) in the plume generated by ArF (193nm, 20ns pulses) excimer laser irradiation of $Bi_2CaSr_2Cu_2O_9$, while only very small peaks were identified as oxide molecules (i.e. BiO and CaO), which appear to be minor constituents in the laser-induced plume from these materials. Contrary to the uncertainties still existing in relation to the type of ablated species for different experimental conditions, a general trend is emerging in that the ablated species from superconducting targets appear to be very energetic, which could significantly contribute to the growth of high quality crystalline films at relatively low (≤ 600 °C) substrate temperature.

An important parameter in laser ablation-deposition of high T_C superconducting films is the laser power (energy) density. At relatively low laser power densities, it is found that the composite target material does not vaporize congruently and the film composition for a given target is dependent on both the laser power and wavelength (Sudarsan et al., 1988). As the power density is increased, the composition of the film more closely approaches that of the target (Geohegan et al., 1988). At very high power levels, the film composition may therefore be less dependent on fluctuations in laser output. However, very high power levels may contribute to the ejection of molten matter from the target as small (~ micron-sized) particles, which are collected on the substrate and could cause difficulties when producing superconducting junctions. A current practice to minimize or avoid the influence of target laser-induced compositional changes on the film stoichiometry involves a continuously rotating target in order to permanently expose a fresh surface to the laser beam (Dijkkamp et al., 1987).

More recently, Singh et al. (1990) analyzed many of the experimental results discussed above in terms of a model developed for simulating the laser deposition process. The model is based on the hypothesis that a high pressure plasma is generated in front of the multicomponent superconductor target upon laser impact on the surface. This plasma is initially confined in a very small volume and subsequently is allowed to suddenly expand into the surrounding vacuum and interact with a substrate located at a certain distance in front of the target. The model includes three separate stages, namely: (i) the interaction of the laser beam with the target surface, (ii) an initial isothermal expansion of the laser-induced plasma, and (iii) a final adiabatic plasma expansion leading to deposition of films. Singh et al.'s (1990) model accurately describes some of the experimental results discussed above. For example, it shows the following:

(1) The highly focused plasma plume component along the target surface normal, observed by several groups (Singh et al., 1988, Venkatesan et al., 1988b, and Auciello, unpublished, 1989) is due to anisotropic expansion velocities of the ablated species in the plume, such that the expansion velocities are related to the initial dimensions and temperature of the plasma, and the atomic weight of the respective species.

(2) The energy density appears to control the maximum plasma temperature, which determines the expansion velocity of the plasma.

(3) Based on simple energy balance considerations, the ion velocities follow a cube root dependence with the energy density (i.e. $v \propto E^{1/3}$), which is in good agreement with limited experimental data on ablation of ZrO_2 by a CO_2 laser beam (Sankur et al., 1987).

(4) The compositional variations in superconducting thin film stoichiometry can be attributed to either non-
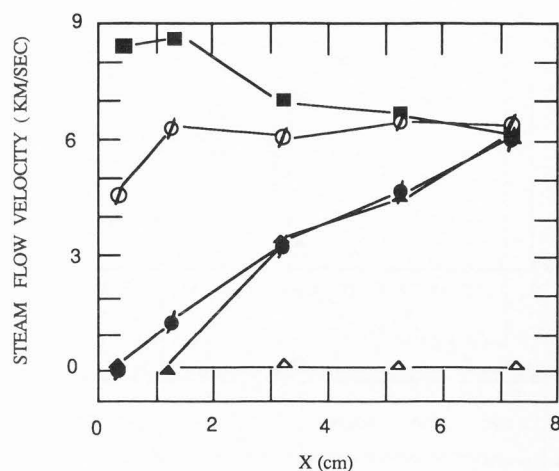

Fig. 14. Dependence of the ablated species velocity on the distance from the target surface along the normal for various species: (■) Cu I, (Ø) Y I, (▲) Ba I, (●) O I, (△) Ba II (Zheng et al., 1989a).

stoichiometric evaporation of the target at low energy densities or to different expansion velocities of the species corresponding to different atomic masses.

The variation of the ablated species' energy as a function of distance from the target, and the angular distribution of the ablated plume, discussed above, may be responsible for changes observed in the deposition rate of Y, Ba, and Cu, when depositing superconducting films by ablation of $YBa_2Cu_3O_7$ targets (Lynds et al., 1987a). This group reported, for example, that the normalized deposition rates for Y, Ba, and Cu were 1, 0.83, and 0.625, respectively, for their particular system. This indicates that a stoichiometric target can produce Y rich films. In fact, films with better stoichiometry have been obtained by using a target stoichiometry of 1:2.4:4.8 (Lynds et al., 1987a).

Some of the characteristics of laser ablation deposition which present problems for laboratory studies may turn out to be advantageous for production purposes. By using large substrates at a correspondingly large target-substrate distance, it may be possible to reduce the deposition rate to a controllable level while at the same time maintaining the laser power density on the target at a level which produces stoichiometric deposition of the thin film material. However, the highly directional nature of the ablated plume, produced by the currently used focused lasers, will probably dictate the necessity of using a planar substrate motion, for the deposition of large area superconducting thin films with relatively uniform thickness and composition. Expensive large beam diameter lasers can help circumvent the need for such a mechanical solution for laser ablation-deposition on large areas. Obviously, further work on this and other areas related to laser ablation-deposition of high T_C superconducting films is necessary to develop this technique to a level compatible with technological applications.

Ion Beam Sputter-Deposition

Ion beam sputter-deposition of high T_C superconducting films has been much less investigated 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.)
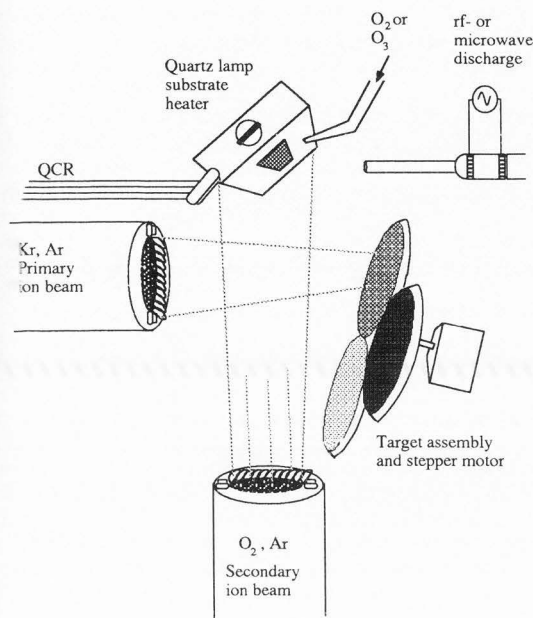
Fig. 15. Schematic of the automated ion beam sputter-deposition system. The computer monitors the quartz crystal resonator (QCR) output, turns the ion beam off, and rotates the targets when the desired amount of sputtered material is deposited (Kingon et al., 1989, and Krauss et al., 1990).

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 (Kobrin et al., 1987). More recently, other researchers have used the ion beam sputter-deposition technique to produce high quality films from sputtering of superconductor targets (Gao et al., 1988), including the production of as-deposited superconducting Y-Ba-Cu-O films (Klein et al., 1989). 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. The technique can, however, yield films with T_c as high as the laser ablation-deposition method and of equal or better quality, and yield higher T_c and better quality films than those produced with the plasma sputter-deposition technique.

More recently, a new automated ion beam sputter-deposition technique has been developed (Krauss and Auciello, 1989, Krauss et al., 1990, Kingon et al., 1989), which has the following features:

(1) High current ion beams generated by either a Kaufman-type (Kaufman et al., 1982) or a capillaritron (Mahoney et al., 1981) ion source, are directed at either 45 ° or near normal incidence with respect to the surface normal (see Fig. 15). Fundamental studies on ion-solid interactions have revealed that the optimun geometry depends on the bombarding ions mass and kinetic energy, and the mass of the sputtered atom being deposited onto the substrate (Ameen et al., 1990).

(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. 15).

(3) A QCR (Fig. 15), 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, and (d) other processing steps.

A specially designed computer program (Krauss and Auciello, 1989) 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 (Kingon et al., 1989). To date, the highest T_c obtained with the automated ion beam sputter-deposition technique is 81 K as measured by the Meissner effect (Krauss et al., 1990). 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, using the TRIM code (Biersack and Haggmark, 1980), studies have recently been initiated in our laboratory, and first results have been published (Ameen et al., 1990, Auciello et al., 1990b). Briefly, these studies have shown that light ions such as Ar^+ impacting at 45º with respect to the target surface normal results in an undesirably high scattered ion flux, involving species with energies as high as about 800 eV, 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 (Ameen et al., 1990, Auciello et al., 1990b). 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.

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 instalation of oxygen sources directed at the substrate, and in-situ ion, electron, and 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 therefore of the sputtering and ion scattering processes. Primary ion scattering can have a major influence on the characteristics of the films, as demonstrated by recent work (Ameen et al., 1990).

(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 Common to Sputter and Vapor-Deposition Techniques

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.

Post-Deposition Annealing and Film Oxygenation

For all techniques described above, a high temperature anneal was necessary to produce superconducting films. $YBa_2Cu_3O_{7-x}$, for example, is unstable for $x \geq 1$, decomposing into Cu metal and yttrium and barium oxides. In practice, therefore, deposition processes occurring at low oxygen activities resulted in amorphous, oxygen-deficient films. The high post-deposition anneal temperatures were necessary, since crystallization into $YBa_2Cu_3O_{7-x}$ requires both cation and anion diffusion. The oxygen stoichiometry of $x=0$ was achieved by a final anneal at an intermediate temperature, or by slowly cooling the film from the high temperature anneal, as discussed below, both processes were conducted in an oxygen atmosphere (Tarascon et al., 1987). The post-deposition heat treatments were similar for all deposition methods.

Films were usually annealed at 850-930 °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 crystallinity of the 123 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 (Hong et al., 1987).

An alternative annealing procedure 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 (Asano et al., 1987). However, some researchers claim, for example, 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 $\geq$ 850 °C are necessary (Dam et al., 1988). 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. 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, Hayasi et al., 1988), post-deposition annealing at relatively low temperatures (350 °C, as claimed by Hayasi et al. (1988), for long periods of time, may produce superconducting films. In fact, Hayasi et al. (1988) claimed that a long annealing at 350 °C resulted in the formation of an orthorhombic structure I which yielded a higher T_c than a similar structure II produced at 550 °C.

Y-Ba-Cu-O superconducting 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) (Naito et al., 1987, Bao et al., 1987, Tsaur et al., 1987, Lathrop et al., 1987, Chan et al., 1987, Qiu and Shih, 1988, Mogro-Campero et al., 1988). Some films deposited under strongly oxidizing conditions, on the other hand, became superconductors after annealing at relatively low temperatures (about 500 °C) (Terashima et al., 1988, Berberich et al., 1988).

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 $SrTiO_3$ presented the sharpest superconducting transition after annealing at 930 °C, but the highest T_c were obtained after heat treatments at 870-900 °C (Chan et al., 1987, Chang et al., 1988, Naito et al., 1987). Conversely, it appears that 920 °C is too high an annealing temperature to produce superconducting films deposited on ZrO_2 (Liou et al., 1987). Ma et al. (1988), on the other hand, claimed that deposited layered structures such as $Cu/BaO/Y_2O_3/Ag/SiO_2$ were transformed into a superconducting film when annealed at 800 °C but not at 750 or 850 °C. Some researchers have suggested that an 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 are also 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 (Sandstrom et al., 1988a). 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 to be considered include:

(a) for films < 1 μm thick, the rate of oxygen intercalation in the lattice is fast enough to go into 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,

(c) an effective oxidation is achieved by heating the films to 400-500 °C in an oxygen atmosphere at a pressure > 0.2 Torr.

216

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 multimetal films (Lee et al., 1987b, Scheuermann et al., 1987, Gurvitch and Fiory, 1987). It is important to distinguish the annealing time and temperature from the oxygenation counterparts. 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 superconducting structure required heating the films above 500 °C (Gurvitch and Fiory, 1987). Other work has shown that the maximum oxygen uptake rate for Y-Ba-Cu films occurs at about 400 °C (Han et al., 1987). 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 SiO_2 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 (Aslam et al., 1988). Ma et al. (1988). 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 SiO_2.

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 $\leq$ 600 °C (Moriwaki et al., 1988), Terashima et al., 1988, Wasa et al., 1988, Witanachchi et al., 1988 and 1989), Margaritondo et al. (Eds.), 1989, Kwo et al. 1988, SPIE, 1988, Miura et al., 1988c). Production of films at substrate temperatures $\leq$ 600 °C is critical for the application of high T_c superconducting films to device technologies, particularly the Si-based semiconductor technology.

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. Witanachchi et al. (1988), 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. 16). 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. (1988) was that atomic oxygen both in neutralized and ionized state created in the oxygenated plasma was dynamically introduced in the growing film,
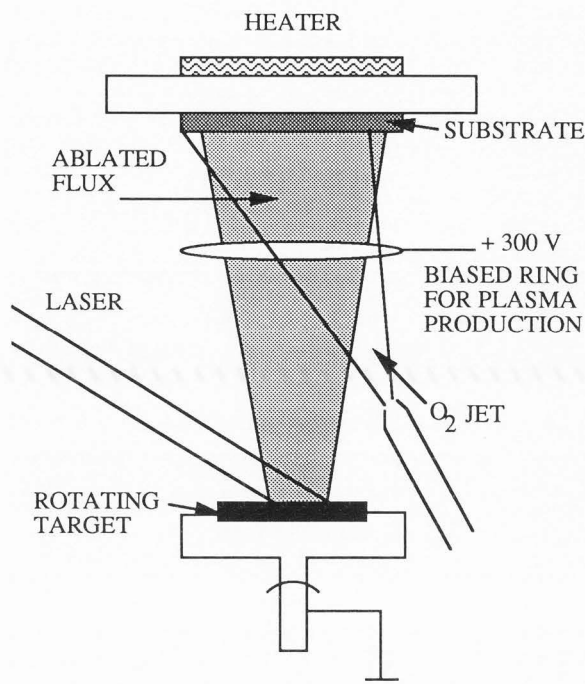

Fig.16. Schematic of the laser ablation-deposition system used for producing as deposited high T_c superconducting films at low substrate temperature (Witanachchi et al., 1988).

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. (1988). Roas et al. (1988), 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 underlaying 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. (1989) 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} cm^2, Koren et al., 1989) than O_2 (the absorption cross section at 193 nm is about 10^{-23} cm^2, Koren et al., 1989). The effective dissociation of N_2O 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. (1989), where a Nd-YAG laser was used to ablate an $YBa_2Cu_3O_{7-x}$ target, while an ArF laser beam, directed parallel to the substrate surface, intersected the ablation plume, during the deposition of films either in an O_2 or an N_2O atmosphere. These experiments demonstrated the following:

(a) Films deposited on $SrTiO_3$ at 600 °C in an O_2 atmosphere, with or without the ArF activation laser, presented a semiconducting behavior without transition to the superconducting state down to 35 K (Fig. 17a), while those deposited in an N_2O 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. 17b).

(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. 17b).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. 17b).

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.

Remarkable progress has recently been made in fabricating as-deposited superconducting films at relatively low substrate temperature, by laser ablation-deposition. Very thin (100 Angstroms) as-deposited superconducting films have been synthesized (Venkatesan et al., 1989), as well superconducting films on Si (Witanachchi et al., 1989a-b, Venkatesan et al., 1989, Wu et al., 1989).

Mizuno et al. (1989) used an $Ar+O_2$ plasma to sputter-deposit polycrystalline Y-Ba-Cu-O films on GaAs (100) with a CaF_2 buffer layer. The substrate temperature was kept at about 450 °C during deposition, and subsequently dropped to 250 °C for 30 minutes followed by an slow cooling down in an O_2 atmosphere after deposition, which produced an as deposited high Tc 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 (1988), Terada et al. (1988). 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. (1988) 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
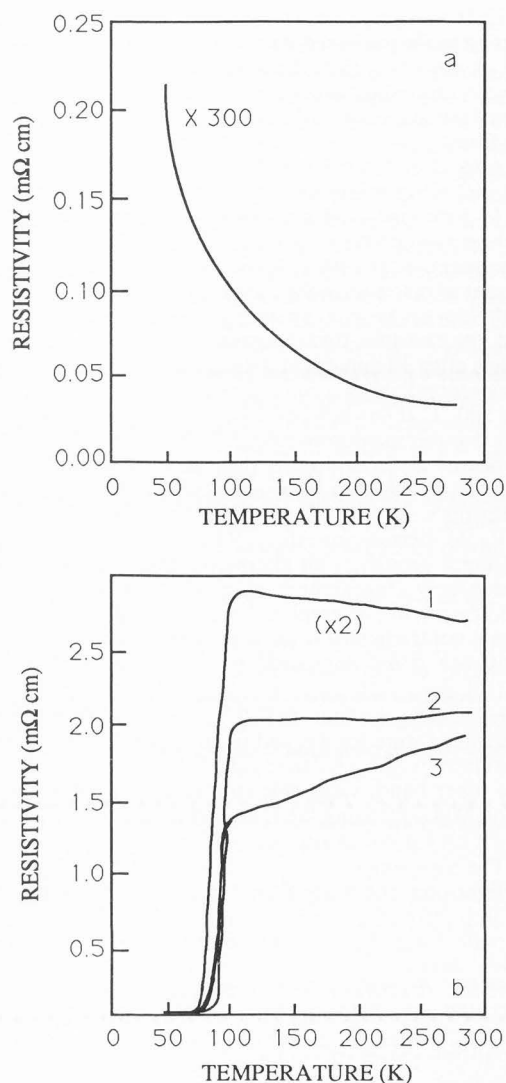

Fig. 17. (a) Resistivity vs. temperature for Y-Ba-Cu-O films deposited on $SrTiO_3$ at 600 °C in 0.2 Torr of O_2 using a Nd:YAG laser (355 nm, 3.2 J/cm^2) to ablate the target, and an ArF (193 nm) excimer laser to irradiate the O_2 gas in front of the target. (b) Same deposition conditions as in (a) but in an N_2O atmosphere; film (1)was deposited without the ArF laser irradiation of N_2O, while (2) and (3) were produced with ArF laser (17 mJ/cm^2) irradiation, time delayed with respect to the ablation laser pulse by 1.6 μs and 10 μs respectively (Koren et al., 1989).

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 $YBa_2Cu_3O_{7-x}$, as demonstrated by Moriwaki et al. (1988) and Aida et al. (1989). 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 O_2^+, 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 $YBa_2Cu_3O_{7-x}$ were produced at substrate temperatures as low as 450 °C.

Aida et al. (1989) also demonstrated that in the case of the evaporation of copper alone, Cu metal is deposited in a molecular oxygen atmosphere (2 x 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. (1989). 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 clearly indicate that the dynamic incorporation of activated oxygen is 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.

Properties of Films

Fundamental properties of films such as transition temperature and width and current carrying capabilities depend largely on stoichiometry and crystalline structure, which can be affected by the film-substrate interaction as well as the substrate crystallography and quality, the latter two including lattice matching to the films and 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

Many materials have been used as substrates, namely: glass, quartz, Si, Al_2O_3, sapphire, gadolinium gallium garnet (GGG), MgO, $2MgO.SiO_2$, Y stabilized cubic ZrO_2, BaF_2, $BaTiO_3$, Ti_9O_{20}, $SrTiO_3$, Sr_2TiO_4, LaGaO, and $LaAlO_3$. Usually, the highest T_c values for $YBa_2Cu_3O_{7-x}$ films, for example, have been obtained with $SrTiO_3$, mainly because the excellent lattice matching. On the other hand, films exhibiting $T_c \geq 70$ K have been synthesized on sapphire (Hong et al., 1987, Scheuermann et al., 1987), MgO (Aida et al., 1989, Adachi et al., 1987, Cuomo et al., 1987, Burbidge et al., 1987), ZrO_2 (Cuomo et al., 1987, Bruyere et al., 1988, Wiesmann et al., 1989), BaF2 (Cuomo et al., 1987, Yee et al., 1987), $BaTiO_3$ (Lee et al., 1987c), Si (Lee et al., 1988), $LaGaO_3$ (Sandstrom et al., 1988b), and $LAlO_3$ (Simon et al., 1988).

A strong interdiffusion of elements at the film-substrate interface can occur in both directions. For example, glass, quartz, Si, and GGG, are reactive substrates, and $YBa_2Cu_3O_{7-x}$ films deposited on them have not shown, generally, superconductivity after a high temperature anneal

(Aida et al., 1989, Houdy et al., 1987, Lin et al., 1988). This may be 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, and Ba and Cu rich layers in the middle and at the film-substrate interface respectively (Lee et al., 1987a). On the other hand, annealing of films deposited on quartz resulted in Cu, Y, and Cu rich, surface, intermediate 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 the reverse diffusion direction, the transport of Si from quartz into $YBa_2Cu_3O_{7-x}$ appears to be stronger than that of Al from sapphire or Mg from MgO (Nakajima et al., 1988). 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. (1988), other researchers (Lee et al., 1988) have recently claimed that they succeeded in producing as-deposited 123 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. On the other hand, post-deposition RTA has yielded superconducting 123 films deposited on Si and SiO_2 substrates (Aslam et al., 1988), and no diffusion of Si into the films was observed.

Al_2O_3, including the sapphire form, have also been used as substrates. Film-substrate reactions have been observed for 123 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., 1987, Shah and Carcia, 1988, Cuomo et al., 1987, Lanchbery, 1988, Bao et al., 1987, Tsaur et al., 1987). 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., 1988). The susbstrate 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., 1988).

The best 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., 1988, de Vries et al., 1988). 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 123 films (Cuomo et al., 1987, Houdy et al., 1987, Nakajima et al., 1988). However, these elements appear to have less effect in relation to suppressing superconductivity in the films, particularly Sr, which substitute Y in the orthorhombic phase.

$LaGaO_3$ and $LaAlO_3$ have been investigated, mainly because of their favorable dielectric properties, which make

them good candidates for applications in certain high frequency devices. These substrates present a relatively good lattice and thermal expansion match to $YBa_2Cu_3O_{7-x}$ films.

Buffer Layers

The 123 films and all ceramic and non-ceramic substrates used until now react with each other at least to some degree. Therefore, researchers have tried to minimize or eliminate that interaction by depositing a buffer layer on top of the substrate. Buffer layers investigated until now include: Cu, Ag, Au, Pt, Nb, Ni, Ti, Vn, NbN, MgO, Y_2O_3, SiO_2, TiO_2, ZrO_2, Ta_2O_5, $SrTiO_3$, $BaTiO_3$ and $MgAl_2O_4$ (Gurvitch and Fiory, 1987, Makous et al., 1987, Lee et al., 1987a, Burbidge et al., 1987, Stamper et al., 1988, Hu et al., 1988, Miura et al., 1988a). 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 123 films, and successful substrate/buffer combinations reported in the literature include ZrO_2/Ag, MgO/Nb, MgO/Ag, and MgO/Au. ZrO_2 seems to be the best buffer layer among those used until now. However, much work is needed to better understand the behavior of and to control the deposition of the buffer layers.

Properties of Vapor-Deposited Films

As with all other deposition techniques, the film stoichiometry significantly affects the T_c as well as the superconducting transition region. It has been demonstrated, for example, that Y-Ba-Cu-O films containing other than the 123 phase present relatively low T_c and wide transition regions in the R vs. T curves. Superconducting 123 films, which have been deposited using evaporation methods, may contain numerous secondary phases. Two of them in particular, CuO and Y_2O_3, have interesting behaviors. Yttrium oxide presents a spherical shape, which does not change upon annealing, suggesting that no reaction occurs between this phase and the rest of the film.

The microstructure of vapor-deposited 123 films may be controlled by synergistic interactions among the deposition parameters. Films have been grown with the c-axis of the perovskite structure either totally or partially parallel or perpendicular to the substrate surface. The control of film orientation is relevant for maximizing the current carrying capabilities of the films, and much work is still needed to understand and control the involved parameters. For example, bilayer structures, including a predominantly single crystalline layer with the c-axis perpendicular to the substrate, and another containing crystals with the c-axis parallel to the substrate, have been found in some vapor-deposited films (Chaudhari et al., 1987b). According to LeGoues (1988), nucleation in post-deposition annealing begins both from the interface and the film surface. At the interface, the substrate forces the film to become epitaxially oriented, while at the surface the nucleation is random. The film orientation depends on the substrate temperature also. For example, 123 films deposited on $SrTiO_3$ presented (110) planes parallel to the surface when grown at 530 °C, while films deposited at substrate temperatures above 600 °C had (103) planes parallel to the surface.

As indicated above, the current carrying capabilities of the superconducting films are largely controlled by the films' microstructure. The highest reported value for the critical current density J_c in vapor-deposited superconducting films presently is 10^6 A/cm^2 at 81 K (Mankiewich et al., 1987). This J_c value was measured on epitaxially grown films. On the other hand, 123 films deposited on Si with a ZrO_2 buffer layer exhibited J_c values of about 5×10^3 A/cm^2 at 4.2 K (Berberich et al., 1988). This lower J_c has been attributed to the random orientation character of the films.

Properties of Sputter-Deposited Films

Sputter-deposited 123 films 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) $SrTiO_3$ substrates (Hirochi et al., 1987, Sandstrom et al., 1988a). Films deposited on (100) $SrTiO_3$ have shown a-axis orientation perpendicular to the substrate. On the other hand, 123 films synthesized on (110) $SrTiO_3$ 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) 123 films have been produced on MgO, ZrO_2, BaF_2, $LaAlO_3$ and $LaGaO_3$ substrates and on oriented Pt buffer layers on Al_2O_3 substrates (Adachi et al., 1987, Yee et al., 1987, Terada et al., 1988, Tanaka and Itozaki, 1988, Hatta et al., 1988, Wiesmann et al., 1989, Sandstrom et al., 1988b, Simon et al., 1988).

Superconductivity in the 123 films described above was highly anistropic and the resistivity was two order of magnitudes larger in the basal plane than along the c axis. Highly oriented sputter-deposited films exhibited J_c of about 10^2 A/cm^2 and 10^4 A/cm^2 at 77 K, parallel and perpendicular to the basal plane respectively (Enamoto et al., 1987). Alternatively, randomly oriented 123 films exhibited J_c values in the range 10^5-10^6 A/cm^2 at 4.2 K and 10^3-10^4 A/cm^2 at 77 K (Silver et al., 1987, Shah and Carcia, 1988). To date, the record J_c measured on sputter-deposited 123 films is 2.54×10^6 A/cm^2 at 77 K, which has been achieved in a highly oriented (001) $HoBa_2Cu_3O_{7-x}$ film deposited on a (001) MgO substrate (Tanaka and Itozaki, 1988). A J_c of about 1.5×10^6 A/cm^2 was maintained in this film even when exposed to a magnetic field of 1.0 T.

Sputter-deposited 123 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 123 phase. A 50% 123 phase is enough to produce a sharp transition, provided that the 123 grains are in contact with each other. Meissner effect measurements, on the other hand, are necessary to determine the total fraction of the superconducting 123 phase in a film. Very few Meissner effect measurements have been reported for sputter-deposited films until now, most of which have shown wide transitions. This indicates that very pure sputter-deposited films are difficult to prepare. Similar comments to those presented above, in relation to Meissner measurements, for sputter-deposited films may apply to other techniques as well.

Properties of Laser Ablation-Deposited Films

Similar to other techniques, the high temperature post-deposition annealing initially used to obtain laser ablation-deposited superconducting films generally resulted in more or less film-substrate interactions, depending on each particular substrate, with the consequent superconductive characteristics degradation. Interface reactions reported in relation to laser ablation-deposited films have followed similar trends as those observed for sputter-deposited films. Compositionally uniform as-deposited films revealed inhomogeneities induced by high temperature annealing. AES depth profiling indicated that Ba is the most mobile ion in the films, followed by Cu.

Laser ablation-deposited 123 films on (100) $SrTiO_3$ and (100) MgO presented a c-axis orientation normal to the substrate surface, whereas less degree of orientation was observed in films deposited on (110) $SrTiO_3$ (Wu et al., 1987b, Miceli et al., 1987, De Santolo et al., 1988, Koren et al., 1988). Films synthesized on Al_2O_3, on the other hand, presented a partial a-axis orientation perpendicular to the substrate surface (Venkatesan et al., 1988c). Films deposited on Si at 600 °C revealed strong (001) XRD lines, which were indicative of the existence of a preferential c-axis orientation perpendicular to the substrate (Wang et al., 1988). This is consistent with the general observation by various researchers that films deposited at relatively low temperature tend to have their c-axis perpendicular to the substrate surface.

Critical temperatures exceeding 77 K have been measured in several laser ablation-deposited films. The onset temperatures have generally been similar to those measured in bulk samples, but the R vs T curves often have presented tails, which were indicative of compositional inhomogeneities across the films. Values of T_c reported in the literature expand the range 45-90 K, depending on the substrate and deposition conditions.

Current densities J_c measured in the first oriented 123 films deposited by laser ablation were about 10^4 A/cm^2 at 4.2 K, lower than those measured in sputter-deposited films. Recently, however, the J_c of laser ablation-deposited films has increased to about 7 x 10^5 A/cm^2 at 77 K (DeSantolo et al., 1988). High quality films were produced by ablation of $BaF_2/Y_2O_3/CuO$ composite targets, followed by high temperature annealing in a moist O_2 atmosphere. Recently, progress has been demonstrated in the quality of as-deposited superconducting 123 films, for which J_c values were in the range 0.7-2.2 x 10^6 A/cm^2 at 77 K (Witanachchi et al., 1988, Witanachchi et al., 1989, Venkatesan et al., 1989). A J_c of 6 x 10^4 A/cm^2 at 77 K has been measured in a 123 film deposited on Si with a double $MgAl_2O_4/BaTiO_3$ buffer layer (Wu et al., 1989).

Properties of Molecular Beam Epitaxy-Deposited Films

As-deposited 123 films generally were insulating and dark but slightly transparent. The films remained stable in air for only 15-20 minutes. Electron diffraction (RHEED) patterns recorded during deposition indicated incomplete oxidation of Cu and growth of metallic Cu microcrystals in a matrix of amorphous Ba and rare earth oxide. The orthorhombic 123 superconducting phase appeared only after post-deposition annealing in flowing oxygen above 750 °C.

Some groups (Schlom et al., 1988, Kwo et al., 1988) have attempted to produce as-deposited superconducting 123 films on different substrates by plasma-assisted oxygenation of the growing films. The as-deposited films did not have, however, good superconducting characteristics, and post-deposition annealing was necessary to increase the oxygen content and improve both T_c and J_c.

MBE-grown 123 films on (100) $SrTiO_3$ have shown strong orientation, with the a-axis perpendicular to the substrate surface, particularly in films containing excess Ba (Kwo et al., 1987). XRD spectra have shown small (005) peaks indicative that c-axis orientation normal to the substrate surface extends to only < 1% of the film. However, the orientation depended, in general, on film stoichiometry, substrate temperature during deposition, and annealing procedure. Films deposited at relatively low substrate temperature (300 °C) presented closer to 123 stoichiometry, for the case of Y-Ba-Cu-O films, and c axis orientation normal to the substrate surface (Webb et al., 1987). The c-axis oriented films presented a higher degree of structural order, lower normal state resistivity and higher J_c than the a-axis oriented ones. Different orientation domains appear to exist in some films, depending on the particular substrates. For example, domains of (110) and (103) orientation have been identified in 123 films deposited on (110) $SrTiO_3$, while a strong (001) orientation has been observed in 123 films deposited on (100) MgO.

The strong orientation observed in MBE-deposited films appears to be a major factor contributing to the relatively high J_c values observed in these films as compared to average sputter or vapor-deposited films. The critical current values were of the order of 10^6 A/cm^2 at 4.2 K and > 10^5 A/cm^2 at 77 K.

Conclusions

A limited review has been presented here on what may be the most promising techniques for production of high T_c superconducting films compatible with relevant technologies such as microelectronics. It is clear that 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 on 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

References

Adachi H, Hirochi K, Setsune K, Kitabatake M, and Wasa K. (1987). Low Temperature Process for the Preparation of High T_c Superconducting Thin Films. Appl. Phys. Lett. **51**, 2263-2265.

Aida T, Tsukamoto A, Imagawa K, Fukazawa T, Sito S, Shindo K, Takagai K, and Miyauchi K. (1989). Thin Film Growth of $YBa_2Cu_3O_{7-x}$ by ECR Oxygen Plasma Assisted Reactive Evaporation. Jpn. J. Appl. Phys. **28**, L635-L638.

Akune T and Sakamoto N. (1988).Y-Ba-Cu-O Thin Films Prepared by DC Magnetron Sputtering. Jpn. J. Appl. Phys. **27**, L2078-2080.

Ameen MS, Auciello O, Rou SH, Soble CS, Graettinger TM, Krauss AR, and Kingon AI. (1990). Studies on Ion Scattering and Sputtering Processes in Ion Beam Sputter-Deposition of High T_C Superconducting Films: Optimization of Deposition Parameters. Amer. Inst. of Phys. Conf. Proc. "High T_C Superconducting Thin Films: Processing, Characterization, and Applications", Stockbauer RL, Krishnaswamy SV, and Kurtz RL (Eds.), No 200, 79-86.

Anderson JB, Andress RP, and Fenn JB. (1966). Studies on the Velocity of Supersonic Molecular Beams. Adv. Chem. Phys. **10**, 275-285.

Asano H, Tanabe K, Katoh Y, Kubo S, and Michikami O. (1987). High T_C Y-Ba-Cu-O Thin Films Prepared by Dual Magnetron Sputtering. Jpn. J. Appl. Phys. **26**, L1221- 1222.

Aslam M, Soltis RE, Logothetis EM, Ager R, Mikkor M, Win H, Chen JT, and Wenger LE.(1988). Rapid Thermal Annealing of Y-Ba-Cu-O Films on Si and SiO_2 SubstratesAppl. Phys. Lett. **53**, 153-155.

Auciello O and Kelly R (Eds.). (1984). "Ion Bombardment Modification of Surfaces: Fundamentals and Applications", Elsevier Science Publishers, The Netherlands.

Auciello O, Athavale S, Hankins OE, Sito M, Schreiner AF, and Biunno N. (1988a). Spectroscopic Analysis of Electronically Excited Species in XeCl Excimer Laser-Induced Plasmas from the Ablated High Temperature Superconductor $YBa_2Cu_3O_7$. Appl. Phys. Lett. **53**, 72-74.

Auciello O, Krauss AR, Santiago-Aviles J, Schreiner AF, and Gruen DM. (1988b). Surface Compositional and Topographical Changes Resulting from Excimer Laser Impacting on $YBa_2Cu_3O_7$ Single Phase Superconductors. Appl. Phys. Lett. **52**, 239- 241.

Auciello O and Krauss AR. (1988c). A Critical Analysis of Deposition Techniques for Production of High Temperature Superconducting Films. Proc. 3rd Intl. Symposium on Surface Science, Salzburg, Austria (reprints available from O. Auciello), p. 197- 203.

Auciello O and Krauss AR. (1989). Proof-of-Principle of a Novel Method for Sputter-Deposition of High T_C Superconductor Films via A Computer-Controlled Mass Analyzed Ion Beam. Amer. Inst. of Phys. Conf. Proc."Thin Film Processing and Characterization of High Temperature Superconductors", Harper JME, Colton RJ, Feldman LC (Eds.) No **165**, 114- 121.

Auciello O, Athavale S, Bourham M, Hankins OE, Gras-Marti A, and Valles-Abarca JA. (1990a). Transport Processes in Plasma-Assisted Deposition of Superconducting Thin Films. Vacuum (in press).

Auciello O, Ameen MS, Krauss AR, Kingon AI, and Ray MA. (1990b). Studies on Ion Scattering and Sputtering Processes in Ion Beam Sputter-Deposition of Multicomponent Oxide Thin Films. Mater. Res. Soc. Conf Proc. (in press, reprints available from O. Auciello).

Bao ZL, Wang FR, Yiang QD, Wang SZ, and Ye ZY, Wu K, Li CY, and Yin DL. (1987). YBaCuO Superconducting Thin Films with Zero Resistance at 84 K by Multilayer Deposition. Appl. Phys. Lett. **51**, 946-947.

Barton RL, Bartholomew CS, Wild WJ, Grieser JL, Marcy HO, and Kannewurf CR. (1987). Laser Deposition of $YBa_2Cu_3O_{7-x}$ Thin Films. Amer. Inst. of Phys. Conf. Proc."Thin Film Processing and Characterization of High Temperature Superconductors", Harper JME, Colton RJ, and Feldman LC (Eds.), No **165**, 166- 173.

Bednorz JG and Muller KA. (1986). Possible High T_C Superconductivity in the Ba-La-Cu-O System. Z. Phys. **B64**, 189-193.

Berberich P, Tate J, Dietsche W, and Kinder H. (1988). Low Temperature Preparation of Superconducting $YBa_2Cu_3O_{7-x}$ Films on Si, MgO, and $SrTiO_3$ by Thermal Co-Evaporation. Appl. Phys. Lett. **53**, 925-926.

Berkeley DD, Johnson BR, Anand N, Beauchamp KM, Conroy LE, Golman AM, Maps J, Mauersberger K, Mecartney ML, Morton J, Touminen M, and Zhang YY-J. (1988). In Situ Formation of Superconducting $YBa_2Cu_3O_7$ Thin Films Using Pure Ozone Vapor Oxidation. Appl. Phys. Lett. **53**, 1973-1975.

Betz G and Wehner GK. (1981). Sputtering of Multicomponent Materials, in "Sputtering by Particle Bombardment, II", Ch.**2,** Berisch R (Ed.), Springer Verlag, p.11-90.

Biersack JP and Haggmark LG. (1980). A Monte Carlo Computer Program for the Transport of Energetic Ions in Amorphous Targets. Nucl. Instr. Meth. **174**, 257-269.

Blamire MG, Morris GW, Someckh RE, and Evetts JE. (1987).Fabrication and Properties of Superconducting Device Structures in $YBa_2Cu_3O_{7-x}$ Thin Films. J. Phys. **D20**, 1330-1335.

Bonch-Bruevich AM and Imas Ya A .(1968). Recoil Momentum and Ejection of Metal Particles Under the Action of Giant Laser Pulses. Sov. Phys. Tech. Phys. **12**, 1407-1409.

Bruyere JC, Marcus J, Reydet PL, Escribe-Fillipini, and Schlenker C. (1988). High T_C Superconducting $YBa_2Cu_3O_{7-x}$ Thin Films Prepared by RF Reactive Sputtering. Mater. Res. Bull. **23**, 429-435.

Bullock DC, Rettner CT, Lee VY, Lim G, Savoy RJ, and Auerback DJ. (1987). Production of Superconducting $YBa_2Cu_3O_x$ Thin Films by DC Diode Sputtering and Annealing. Amer. Inst. of Phys. Conf. Proc. "Thin Film Processing and Characterization of High Temperature Superconductors", Harper JME, Colton RJ, and Feldman LC (Eds.), No **165**, 71-78.

Burbidge D, Mulhern P, Dew S, and Parsons R. (1987). Sputter-Deposition of Y-Ba-Cu-O Compound System. Amer. Inst. of Phys. Conf. Proc. "Thin Film Processing and Characterization of High Temperature Superconductors", Harper JME, Colton RJ, and Feldman LC (Eds.), No **165**, 87-94.

Chan S, Greene LH, Feldman WL, Miceli PF, and Bagley BG. (1987). The Preparation of Superconducting Thin Films of $YBa_2Cu_3O_{7-x}$ by Co-Evaporation with Electron-Beam/Thermal Sources. Amer. Inst. of Phys. Conf. Proc."Thin Film Processing and Characterization of High Temperature Superconductors", Harper JME, Colton RJ, and Feldman LC (Eds.), No **165**, 28-35.

Chang C, Tsuei CC, Chi CC, and McGuire TR. (1988). Thin Film Y-Ba-Cu-O Superconductor Formed by Cu/BaO/Y_2O_3 Appl. Phys. Lett. **52**, 72-74.

Chaudhari P, Koch RH, Laibowitz RB, McGuire TR, and Gambino RJ. (1987a). Critical Current Measurements in Epitaxial Films of $YBa_2Cu_3O_{7-x}$ Compound. Phys. Rev. Lett. **58**, 2684-2686.

Chaudhari P, Collins RT, Freitas P, Gambino RJ, Kirtley JR, Kock RH, Laibowitz RB, LeGoues FK, McGuire TR, Penney T, Schlesinger Z, Segmuller AP, Foner S, and McNiff EG, Jr.(1987b). Properties of Epitaxial Films of $YBa_2Cu_3O_{7-x}$. Phys. Rev. **B36**, 8903-8906.

Cuomo JJ, Chisholm MF, Yee DE, Mikalsen DJ, Madakson PB, Roy RA, Giess E, and Scilla G. (1987). Substrate Effect on the Superconductivity of $YBa_2Cu_3O_7$ Thin Films. Amer. Inst. of Phys. Conf. Proc."Thin Film Processing and Characterization of High Temperature Superconductors", Harper JME, Colton RJ, and Feldman LC (Eds.), No **165**, 141-148.

Dam B, Baller TS, van Veen GNA, van Hal HAM, de Vries JWC, and Stollman GM. (1988). Interface Effect of Laser Ablated and Sputtered high T_C Superconducting Thin Films. Mater. Res. Soc. Symp. Proc. "High Temperature Superconductors", Brodsky MB, Dynes RC, Kitazawa K, and Tuller HL (Eds.), vol. **99**, 319-325.

DeSantolo AM, Mandich ML, Sunshine S, Davidson BA, Fleming RM, Marsh P, and Kometani TY. (1988). Preparation of High T_c and J_c Films of (123) Using Laser Evaporation of a Composite Target Containing BaF_2. Appl. Phys. Lett. **52**, 1995-1997.

Deshmukh S, Rothe EW, Reck GP, Kushida T, and Xu ZG. (1988). Emission Spectra from ArF laser ablation of High T_c Superconductor $Bi_2CaSr_2Cu_2O_7$. Appl. Phys. Lett. **53**, 2698-2700.

De Vries JWC, Dam B, Heijman MGJ, Stollman GM, Gijs MAM, Hagen CW, and Griessen RP. (1988). Preparation, Patterning and Properties of Thin (123) Films. (1988). Appl. Phys. Lett. **52**, 1904-1906.

Dijkkamp D, Venkatesan T, Wu XD, Shaheen SA, Jisrawi N, Min-Lee YH, McLean WL, and Croft M. (1987). Preparation of Y-Ba-Cu Oxide Superconductor Thin Films Using Pulsed Laser Evaporation from High T_c Bulk Material. Appl. Phys. Lett **51**, 619- 621.

Enamoto Y, Murakami T, Suzuki M, and Moriwaki K. (1987). Largely Anisotropic Superconducting Critical Current in Epitaxially Grown $YBa_2Cu_3O_{7-x}$ Thin Films. Jpn. J. Appl. Phys. **26**, L1248-1250.

Eom CB, Sun JZ, Yamamoto K, Marshall AF, Luther KE, Geballe TH, and Laderman SS. (1989). In Situ (123) Thin Films from Single Target Magnetron Sputtering. Appl. Phys. Lett. **55**, 595-597.

Eryu O, Murakami K, Takita K, Masuda K, Uwe H, Kudo H, and Sakudo T.(1988). Y-Ba-Cu-Oxide Films Formed with Pulsed-Laser Induced Fragments. Jpn. J. Appl. Phys. **27**, L628-631.

Fisanick GJ, Brasen D, Opila R, Moore R, Mankiewich P, Skocpol W, Howard RE, Hong M, and O'Bryan HM. (1987). CW Laser Etching of $YBa_2Cu_3O_7$ Films. Amer. Inst. of Phys. Conf. Proc. "Thin Film Processing and Characterization of High Temperature Superconductors", Harper JME, Colton RJ, and Feldman LC (Eds.), No **165**, 189-196.

Gagliano FP and Paek UC. (1974). Observation of Laser-Induced Explosion of Solid Materials and Correlation with Theory. Appl. Opt. **13**, 274-279.

Gao J, Zhang YZ, Zaho BR, Out P, Yuan CW, and Li L. (1988). High T_c Y-Ba-Cu-O Thin Films by Ion Beam Sputtering. Appl. Phys. Lett. **53**, 2675-2676.

Gawalek W, Michalke W, Bruchlos H, Eick T, Hergt R, and Schmidt G. (1988). Preparation of High T_c Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O Thin Films by RF Magnetron Sputtering. Phys. Status. Solidi **A109**, 503-509.

Geohegan DB, Mashburn DN, Culbertson RJ, Pennycook SJ, Budai JD, Valiga RD, Sales BC, Lowndes DH, Boatner LA, Sondner E, Eres D, Christen DK, and Christie WH. (1988) .Pulsed Laser Ablation of Thin Superconducting Films of $Ho_1Ba_2Cu_3O_{7-x}$ and $Y_1Ba_2Cu_3O_{7-x}$. J. Mater. Res. **3**, 1169-1179.

Geohegan DB and Mashburn DN. (1989). Characterization of Ground-State Neutral and Ion Transport During Laser Ablation of $YBa_2Cu_3O_{7-x}$ Using Transient Optical Absorption Spectroscopy. Appl. Phys. Lett. **55**, 2345-2347.

Ginley DS, Kwak JF, Hellmer RP, Baughman RJ, Venturini EL, and Morosin B. (1988). Sequential Electron Beam Evaporated Films of $Tl_2CaBa_2Cu_2O_y$ with Zero Resistance at 97 K. Appl. Phys. Lett. **53**, 406-408.

Goto T, Masumoto M, and Toshio H. (1989). Preparation of Superconducting $YBa_2Cu_3O_{7-x}$ Films by ECR Plasma Sputtering. Jpn. J. Appl. Phys. **28**, L88-90.

Gurvitch M and Fiory AT. (1987). Preparation and Substrate Reactions of Superconducting Y-Ba-Cu-O Films. Appl. Phys. Lett. **51**, 1027-1029.

Hammond RH, Naito M, Oh M, Hanh B, Rosenthal M, Marshall P, Missert N, Beasley MR, Kapitulnik A, and Geballe TH. (1988). Superconducting Thin Films of the Perovskite Superconductors by Electron Beam Deposition. Mater. Res. Soc. Symp. Proc. "High Temperature Superconductors", Brodsky MB, Dynes RC, Kitazawa K, Tuller HL (Eds.), vol 99, 169-171.

Han Z, Bourget L, Li H, Ulla M, Millman WS, Baum HP, Xu MF, Sarma BK, Levy M, and Tonner BP. (1987).Single Target Sputter-Deposition, Post-Processing and Electron Spectroscopy of Perovskite Superconductor Thin Films. Amer. Inst. of Phys. Conf. Proc."Thin Film Processing and Characterization of High Temperature Superconductors", Harper JME, Colton RJ, Feldman LC (Eds.), No **165**, 66-70.

Harper JME, Colton RJ, and Feldman LC, (Eds.). (1988). American Vacuum Society Topical Conference Proceedings on "Thin Film Processing and Characterization of High Temperature Superconductors". Amer. Inst. of Phys. Conf. Proc., No **165**.

Hatou T, Takai Y, and Hayakawa H. (1988).Y-Ba-Cu-O Superconducting Thin Film Prepared by Flash Evaporation. Jpn. J. Appl. Phys.**27**, L617-618.

Hatta S, Higashino H, Hirochi K, Adachi H, and Wasa K. (1988). Pt-Coated Substrate effect on Oxide Superconductive Films in Low Temperature Processing. Appl. Phys. Lett. **53**, 148-150.

Hayashi S, Kamada T, Setsune K, Hirao T, Wasa K, and Matsuda A. (1988). The Orthorhombic-2-Tetragonal Phase Transition in Sputter-Gd-Ba-Cu-O Thin Films by Low Temperature Processing. Jpn. J. Appl. Phys. **27**, L1257-1259.

Hirochi K, Adachi H, Setsune K, Yamazaki O., and Wasa K. (1987). Thickness Dependence of Superconductivity in as-Sputtered Er-Ba-Cu-O Thin Films. Jpn. J. Appl. Phys. **26**, L1837-1838.

Hong M, Liou S.H., Kwo J., and Davidson B.A. (1987). Superconducting Y-Ba-Cu-O Oxide Films by Sputtering. Appl. Phys. Lett. **51**, 694-696.

Hong M, Liou SH, Bacon DD, Grader GD, Kwo J, Kortan AR, and Davidson BA. (1988). Superconducting Tl-Ba-Ca-Cu-O Films by Sputtering. Appl. Phys. Lett. **53**, 2102-2104.

Houdy P, Sirat JA, Theeten JB, Landesman JP, Baudry H, Monneraye M, Schiller C, and Patillon JN. (1987). Amorphization Evidence from Kinetic Ellipsometry in Monolayer Controlled Deposition of RF Sputtered YBaCuO Compounds. Amer. Inst. of Phys. Conf. Proc."Thin Film Processing and Characterization of High Temperature Superconductors", Harper JME, Colton RJ, and Feldman LC (Eds.), No **165**, 122-129.

Hu R, Jiang C, and Luo HL. (1988). RF Sputter-Deposition of $YBa_2Cu_3O_{7-x}$ Superconducting Thin Films. Mater. Res. Bull. **23**, 1159-1162.

Kamada T, Setsune K, Hirao T, and Wasa K. (1988). Structure and Superconducting Properties of Sputtered Gd-Ba-Cu-O Thin Films. Appl. Phys. Lett. **52**, 1726-1728.

Kang JH, Kampwirth RT, Gray KE, Marsh S, and Huff EA. (1988a). Superconductivity in Thin Films of the Bi-Ca-Sr-Cu-O System. Phys. Lett. **A128**, 102-104.

Kang JH, Kampwirth RT, and Gray KE. (1988b). Superconductivity in Sputtered Thin Films of Tl-Ba-Ca-Cu-O. Phys. Lett. **A131**, 208- 210.

Kang JH, Kampwirth RT, and Gray KE. (1988c).High Critical Field Anisotropy of Superconducting Ba-Sr-Ca-Cu Oxides from Highly Oriented Thin Films. Appl. Phys. Lett. **52**, 2080-2082.

Kanai M, Kawai T, Kawai S, and Tabata H. (1989). Low Temperature Formation of Multilayered Bi(Pb)-Sr-Ca-Cu-O Thin Films by Successive Deposition Using Laser Ablation. Appl. Phys. Lett. **54**, 1802-1804.

Kaufman HR, Cuomo JJ, and Harper JME. (1982). Technology and Applications of Broad-Beam Ion Sources Used in Sputtering. Part I. Ion Source Technology. J. Vac. Sci. Technol. **21**, 725-736.

Kawai T, Kanai M, and Kawai M. (1988). Laser Ablation Multilayered-Deposition of High Temperature Superconducting Films. Mater. Res. Soc. Symp. Proc., Brodsky MB, Dynes RC, Kitazawa K, and Tuller HL (Eds.), vol. **99**, 327-332.

Kelly R and Dreyfus RW. (1988).Reconsidering the Mechanism of Laser Sputtering with Knudsen-Layer Formation Taken into Account. Nucl. Instr. Meth. Phys. Res. **B32**, 341-348.

Kingon AI, Auciello O, Ameen MS, Rou SH,and Krauss AR. (1989).YBa$_2$Cu$_3$O$_{7-x}$ Films Deposited by a Novel Ion Beam Sputtering Technique. Appl. Phys. Lett. **55**, 301-303.

Klein JD and Yen A. (1990). The Influence of r.f. sputter variables on the composition of YBa$_2$Cu$_3$O$_7$ Films. J. Vac. Sci. Technol. **A 8**, 1-6.

Klein JD, Yen A, and Clauson SL. (1989). Ion Beam Deposition of *in situ* Superconducting Y-Ba-Cu-O Films. Appl. Phys. Lett. **56**, 394-396.

Kobrin PH, DeNatale JF, Housley RM, Flintoff JF, and Harber AB. (1987). Superconducting Oxide Thin Films by Ion Beam Sputtering. Advanced Ceramic Materials **2**,430-435.

Komuro S, Aoyagi Y, Morikawa T, and Namba S. (1988). Preparation of High T$_c$ Superconducting Films by Q-Switched YAG Laser Sputtering. Jpn. J. Appl. Phys. **27**, L34-36.

Koren G, Polturak E, Fisher B, Cohen D, and Kimel G. (1988). Highly Oriented As-Deposited Superconducting Laser Ablated Thin Films of YBa$_2$Cu$_3$O$_{7-x}$ on SrTiO$_3$, Zirconia, and Si Substrates. Appl. Phys. Lett. **53**, 2230-2232.

Koren G, Gupta A, and Baseman RJ. (1989). Role of Atomic Oxygen in the Low Temperature Growth of (123) Thin Films by Laser Ablation-Deposition. Appl. Phys. Lett. **54**, 1920-1922.

Krauss AR and Auciello O. (1990). U.S. Patent No 4,923,585, "Automated Ion and Laser Beam Sputter-Deposition Systems for Production of Multicomponent and Multilayered Films."

Krauss AR, Auciello O, Kingon AI, Ameen MS, Barr T, and Liu YL. (1990). Computer-Controlled Ion and Laser Beam Sputter- and Ablation-Deposition Systems for Synthesizing Muticomponent Oxide Films. Rev. Sci. Instr. (in press).

Kwo J, Hsieh TC, Flemming RM, Hong M, Liou SH, Davidson BA, and Feldman LC. (1987). Structural and Superconducting Properties of Orientation/Ordered YBa$_2$Cu$_3$O$_{7-x}$ Films Prepared by Molecular Beam Epitaxy. Phys. Rev. **B36**, 4039-4042.

Kwo J, Hong M, Trevor DJ, Fleming RM, White AE, Farrow RC, Kortan AR, and Short KT. (1988). In-Situ Epitaxial Growth of YBa$_2$Cu$_3$O$_{7-x}$ Films by Molecular Beam Epitaxy with an Activated Oxygen Source. Appl. Phys. Lett. **53**, 2683-2685.

Kwok HS, Mattocks P, Shi L, Wang XW, Witanachchi S, Ying QY, Zheng JP, and Shaw DT. (1988). Laser Evaporation-Deposition of Superconducting and Dielectric Thin Films. Appl. Phys. Lett. **52**, 1825-1827.

Laibowitz RB, Koch RH, Chaudari P, and Gambino RJ. (1987). Thin Superconducting Oxide Films. Phys. Rev. **B35** , 8821- 8823.

Lanchbery JF. (1988). The Formation of Thin Y-Ba-Cu-O Oxide Films by RF Sputtering. J. Phys. **D21**, 538-541.

Lathrop DK, Russek SE, and Buhrman RA. (1987). Production of YBa$_2$Cu$_3$O$_{7-x}$ Superconductor Thin Films *in situ* by High Pressure Reactive Evaporation and Rapid Thermal Annealing. Appl. Phys. Lett. **51**, 1554-1556.

Lee SY, Murdock B, Chin D, and Van Duzer T. (1987a). Microprobe Characterization of Sputtered High T$_c$ Superconducting Films on Silicon. Amer. Inst. of Phys. Conf. Proc."Thin Film Processing and Characterization of High Temperature Superconductors", Harper JME, Colton RJ, and Feldman LC (Eds.), No **165**, 427-434.

Lee SJ, Rippert ED, Jin BY, Song SN, Hwu SJ, Poppelmeier K, and Ketterson JB.(1987b). Preparation of Y-Ba-Cu-O Thin Films on MgO by DC Magnetron Sputtering from a Stoichiometric YBa$_2$Cu$_3$O$_{7-x}$ Target.

Appl. Phys. Lett. **51**, 1194-1196.

Lee WY, Salem J, Lee V, Retter CT, Lim J, Savoy R, and Deline V. (1987c). High T$_c$ YBa$_2$Cu$_3$O$_{7-x}$ Superconducting Thin Films by RF Magnetron Sputtering. Amer. Inst. of Phys. Conf. Proc."Thin Film Processing and Characterization of High Temperature Superconductors", Harper JME, Colton RJ, and Feldman LC (Eds.), No **165**, 95-105.

Lee WY, Salem J, Lee V, Huang T, Savoy R, Deline V, and Duran J. (1988). High T$_c$ YBa$_2$Cu$_3$O$_{7-x}$ Thin Films on Si Substrates by DC Magnetron Sputtering from Stoichiometric Oxide Targets. Appl. Phys. Lett. **52**, 2263-2265.

LeGoues FK. (1988). The Microstructure of YBa$_2$Cu$_3$O$_{7-x}$ Oxide Thin Films on SrTiO$_3$ Substrates. Philos. Mag. **B57**, 167-177.

Li HC, Linker G, Ratzel F, Smithey R, and Geerk J. (1988). In Situ Preparation of YBa$_2$Cu$_3$O$_{7-x}$ Superconducting Thin Films by Magnetron Sputtering. Appl. Phys. Lett. **52**, 1098-1100.

Lin RJ, Chen YC, Kung JH, and Wu PT. (1988). Preparation of Y-Ba-Cu-O Superconducting Films by Modified DC Sputtering Processes. Mater. Res. Soc. Symp. Proc. "High Temperature Superconductors", Brodsky MB, Dynes RC, Kitazawa K, and Tuller HL (Eds.), vol. **99**, 319-325.

Liou SH, Hong M, Davidson BA, Farrow RC, Kwo J, Hsieh TC, Fleming RM, Chen HS, Feldman LC, Kortan RA, and Felder RJ. (1987).High T$_c$ Superconducting Y-Ba-Cu-O Oxide Films by Sputtering and Molecular Beam Epitaxy: Morphology, Structural Characterization and Superconducting Properties. Amer. Inst. of Phys. Conf. Proc. "Thin Film Processing and Characterization of High Temperature Superconductors", Harper JME, Colton RJ, and Feldman LC (Eds.), No **165**, 79-86.

Liou SH, Hong M, Kwo J, Davidson BA, Chen HS, Makahara S, Boone T, and Felder RJ. (1988). Y-Ba-Cu-O Films by RF Magnetron Sputtering using Single Composite Targets: Superconducting and Structural Properties. Appl. Phys. Lett. **52**, 1735-1737.

Lynds L, Weinberger BR, Peterson GG, and Kranski HA. (1987a). Superconducting Thin Films of Y-Ba-Cu-O Produced by Nd: Yttrium, Aluminum, Garnet Laser Ablation. Appl. Phys Lett. **52**, 320-322.

Lynds L, Weinberger BR, and Grudkowski TW. (1987b). High T$_c$ Superconducting Thin Films Prepared by Pulsed Nd:YAG Laser Ablation. Amer. Inst. of Phys. Conf. Proc. "Thin Film Processing and Characterization of High Temperature Superconductors", Harper JME, Colton RJ, and Feldman LC (Eds.), No **165**, 159-165.

Ma LY, Licata TJ, Wu X, Yang ES, and Chang C. (1988). High T$_c$ Superconducting Thin Film by Rapid Thermal Annealing of Cu/BaO/Y$_2$O$_3$ Layered Structures. Appl. Phys. Lett. **53**, 2229-2231.

Maeda H, Tanaka T, Fukutomi M, and Asano T. (1988). A New High T$_c$ Oxide Superconductor Without a Rare Earth Element. Jpn J. Appl. Phys. **27**, L209-210.

Mahoney JF, Pereel J, and Forrester AT. (1981). Capillaritron: A New Versatile Ion Source. Appl. Phys. Lett. **38**, 320-323.

Makous JL, Maritato L, Falco CM, Cronnin JP, Rajendran GP, Uhlmann EV, and Uhlmann DR. (1987). Superconducting and Structural Properties of Sputtered Thin Films of YBa$_2$Cu$_3$O$_{7-x}$. Appl. Phys. Lett. **51**, 2164-2166.

Mankiewich PM, Scofield JH, Skocpol WJ, Howard RE, Dayem AH, and Good E. (1987). Reproducible Technique for Fabrication of Thin Films of High Transition Temperature Superconductors. Appl.Phys. Lett. **51**, 1753-1755.

Margaritondo G, Joynt R, and Onellion M (Eds.). (1989). High T$_c$ Superconducting Thin Films, Devices, and Applications. Amer. Inst. of Phys. Conf. Proc. No **182**.

Mashburn DN, Geohegan DB, Eres D, Lowdnes DH, Boatner LA, Sales BC, Pennycook SJ, Culbertson RJ,

Sondere E, and Christen DK.(1988). Deposition of High T_c Superconductor Thin Films by Pulsed Laser Ablation. Mater. Res. Soc. Sympos. Proc. "High Temperature Superconductors", Broadsky MB, Dynes RC, Kitazawa K, and Tuller HL (Eds.), vol **99**, 699-705.

May P, Jedamzik D, Boyle W, and Miller P.(1988). Production of Superconducting Thick Films by a Spin-on Process, Supercond. Sci. Technol. **1**, 1-4.

Miceli PF, Venkatesan T, Wu KD, and Potenza JA. (1987).X-Ray Diffraction Study of Laser Deposited High T_c Thin Films on (001) SrTiO$_3$. Amer. Inst. of Phys. Conf. Proc. "Thin Film Processing and Characterization of High Temperature Superconductors", Harper JME, Colton RJ, and Feldman LC (Eds.), No **165**, 150-158.

Michikami O, Asano H, Katoh Y, Kubo S, and Tanabe K. (1987). Synthesis of Y-Ba-Cu-O Thin Films on Sapphire Substrates by RF Magnetron Sputtering. Jpn. J. Appl. Phys. **26**, L1199-1201.

Miura S, Terashima Y, Sagoi M, and Kubo K. (1988a). Low Temperature Preparation of As-Sputtered Superconducting YBaCuO Thin Films by Magnetron Sputtering. Jpn. J. Appl. Phys. **27**, L1260-1261.

Miura S, Yoshitake T, Satoh T, Miyasaka Y, and Shohata N. (1988b). Structure and Superconducting Properties of YBa$_2$Cu$_3$O$_{7-x}$ Films Prepared by Transversely Excited Atmospheric Pressure CO$_2$ Pulsed Laser Evaporation. J. Appl. Phys.**52**, 1008-1010.

Miura S, Yoshitake T, Matsubara S, Miyasaka Y, Shohata N, Satoh T. (1988c). Epitaxial Y-Ba-Cu-O Films on Si with Intermediate Layer by RF Magnetron Sputtering. Appl. Phys. Lett. **53**, 1967-1969.

Mizuno K, Miyauchi M, Setsune K, and Wasa K. (1989). Low Temperature Deposition of Y-Ba-Cu-O Films on CaF$_2$/GaAs Substrates. Appl. Phys. Lett.**54**, 383- 385.

Mochiku T, Kanke Y, Wen Z, Iguchi Y, and Yamaka Y. (1988). Effect of Substrate Temperature on the Crystalline State of Ba$_2$ErCu$_3$O$_{7-x}$ Superconducting Thin Films by RF Magnetron Sputtering. Jpn. J. Appl. Phys. **27**, L1679-1682.

Mogro-Campero A, Hunt BD, Turner LG, Burrel MC, and Balz WE. (1988). Y-Ba-Cu-O Superconducting Thin Films by Simultaneous or Sequential Evaporation. Appl. Phys. Lett. **52**, 584-586.

Mogro-Campero A and Turner LG. (1988). Thin Films of Y-Ba-Cu-O on Silicon and Silicon Dioxide. Appl. Phys. Lett. **52**, 1185-1186.

Moriwaki K, Enamoto Y, Kubo S, and Murakami T. (1988). As-Deposited Superconducting Ba$_2$YCu$_3$O$_{7-y}$ Films Using ECR Ion Beam Oxidation. Jpn. J. Appl. Phys. **27**, L2075-L2077.

Naito M, Hammond RH, Oh B, Hahn MR, Hsu JWP, Rosenthal P, Marshall AF, Beasley MR, Geballe TH, and Kapitulnik A. (1987).Thin Film Synthesis of the High T_c Oxide Superconductor YBa$_2$Cu$_3$O$_7$ by Electron Beam Co-Deposition. J. Mater. Res. **2**, 713-725.

Nakajima H, Yamaguchi S, Iwasaki K, Morita H, Fujimory H, and Fujino Y. (1988). Interdiffusion and Interfacial Reaction Between an YBa$_2$Cu$_3$O$_x$ Thin Film and Substrates. Appl. Phys. Lett. **53**, 1437-1439.

Narayan J, Biunno N, Singh R, Holland OW, and Auciello O. (1987). Formation of Thin Superconducting Films by a Laser Processing Method. Appl. Phys. Lett. **51**, 1845- 1847.

Nastasi M, Arendt PN, Tesmer JR, Maggiore CJ, Cordi RC, Bish DL, Thompson JD, Cheong SW, Bordes N, Smith JF, and Raistrick ID. (1987). Fabrication of Oxide Superconductors from Multilayered Metallic Thin Films. J. Mater. Res. **2**, 726-731.

Oh B, Naito M, Arnason S, Rosental P, Barton R, Beasley MR, Geballe TH, Hammond RH, and Kapitulnik A. (1987). Critical Current Densities and Transport in Superconducting YBa$_2$Cu$_3$O$_{7-x}$ Films Made by Electron Beam Evaporation. Appl.Phys. Lett. **51**, 852-854.

Ohkuma H, Mochiku T, Kanke Y, Wen Z, Yokoyama S. (1987). Preparation of Y-Ba-Cu-O Thin Films by RF Magnetron Sputtering. Jpn J. Appl. Phys. **26**, L1484-1486.

Onuma Y, Kamimura K, Nkao M, Kunugi K, and Kubota M. (1988). Y-Ba-Cu-O Thin Films Formed on Alumina Ceramic Substrates Coated with Yttria Stabilized Zirconia Layer. Jpn. J. Appl. Phys. **27**, 1351-1352.

Qiu CX and Shih I. (1988). Thin Films Prepared by a Multilayer Vacuum Method. Appl. Phys. Lett. **52**, 587-589.

Roas B, Schultz L, and Endres G. (1988). Epitaxial Growth of YBa$_2$Cu$_3$O$_{7-x}$ Thin Films by Laser Evaporation Process. Appl. Phys. Lett. **53**, 1557-1559.

Rossnagel SM and Cuomo JJ. (1988). Negative Ion Effects During Magnetron and Ion Beam Sputtering of YBa$_2$Cu$_3$O$_7$. Amer. Inst. of Phys. Conf. Proc. "Thin Film Processing and Characterization of High Temperature Superconductors", Harper JME, Colton RJ, and Feldman LC (Eds.), No **165,** 106- 113.

Sandstrom RL, Gallagher WJ, Dinger TR, Koch RH, Laibowitz RB, Kleinsasser AW, Gambino RJ, Bumble B, and Chisholm MF. (1988a). Reproducible Single Target Sputtering Process for High Temperature Superconducting Films and Devices. Appl. Phys. Lett.**53**, 444-446.

Sandstrom RL, Giess EA, Gallagher WJ, Segmuller A, Cooper EI, Chisholm MF, Gupta S, Shinde S, and Laibowitz RB. (1988b). Lanthanum Gallate Substrates for Epitaxial High Temperature Superconducting Thin Films. Appl. Phys. Lett. **53**, 1874-1876.

Sankur H, Denatale J, Gunning W, Nelson JG. (1987). Dense Crystalline ZrO$_2$ Thin Films Deposited by Pulsed Laser Evaporation. J. Vac. Sci. Technol. A**5**, 2869-2874.

Schellingerhout AJG, van de Leur RHM, Scahlkoord D, van der Marel D, and Mooij JE. (1988). Analysis of YBa$_2$Cu$_3$O$_{7-x}$ Thin Films on Sapphire Substrates Made by Electron Beam Evaporation. Z. Phys. B**71**, 1-5.

Scheuermann M, Chi CC, Tsuei CC, Yee DS, Cuomo JJ, Laibowitz RB. (1987). Magnetron Sputtering and Laser Patterning of High Transition Temperature Cu Oxide Films. Appl. Phys. Lett. **51**, 1951-1953.

Schlom DG, Eckstein JN, Hellman ES, Streiffer SK, Harris JS, Beasley MR, Jr, Bravman JC, Geballe TH, Webb C, Von Dessonneck KE, and Turner F. (1988). Molecular Beam Epitaxy of Layered Dy-Ba-Cu-O Compounds. Appl. Phys. Lett. **53**, 1660-1662.

Shah SI and Carcia PF. (1988). Growth of YBa$_2$Cu$_3$O$_{7-x}$ Thin Films by Sputtering. Amer. Inst. of Phys. Conf. Proc. "Thin Film Processing and Characterization of High Temperature Superconductors", Harper JME, Colton RJ, and Feldman LC (Eds.), No **165**, 50-57.

Sheng ZZ and Hermann AM. (1988). Bulk Superconductivity at 120 K in the Tl-Ca/Ca-Cu-O System. Nature **332**, 138-139.

Silver RM, Talvacchio J, and de Lozanne AL. (1987). Sputter-Deposition of YBa$_2$Cu$_3$O$_{7-x}$ Thin Films. Appl. Phys. Lett. **51**, 2149-2151.

Simon RW, Platt CE, Lee AE, Lee GS, Daly KP, Wire MS, Luine JA, and Urbanik M.(1988). Low-Loss Substrate for Epitaxial Growth of High Temperature Superconductor Thin Films. Appl. Phys. Lett. **53**, 2677-2679.

Singh RK, Biunno N, Narayan J. (1988). Microstructural and Compositional Variations in Laser-Deposited Superconducting Thin Films. Appl. Phys. Lett. **53**, 1013-1015.

Singh RK, Holland OW, Narayan J. (1990). Theoretical Model for Deposition of Superconducting Thin films Using Pulsed Laser Evaporation Technique. J. Appl. Phys. (in press).

Sorimachi Y, Kobayashi A, Yamashita T, Takata M, Miyauchi S, and Tsubata I. (1987). Formation of Superconducting Y-Ba-Cu-O Thin Films by the Solid Phase

Reaction Between $BaCo_3/Cu/Y_2O_3$ Layers on Single Crystalline $SrTiO_3$ Substrates. Jpn. J. Apl. Phys. **26**, L1451-1452.

SPIE-Int. Soc. Opt. Eng. (USA). (1988). High T_c Superconductivity: Thin Films and Devices, vol. **948**.

Stamper A, Greve DW, Wong D, and Schlesinger TE. (1988).Sputter-Deposition of $YBa_2Cu_3O_{6+x}$ on Alumina and the Influence of ZrO_2 Buffer Layers. Appl. Phys. Lett. **52**, 1746-1748.

Sudarsan U, Cody NW, Bozack MJ,and Solanki R. (1988). Excimer Laser-Induced Sputtering of $YBa_2Cu_3O_7$, J. Mater. Res. **3**, 825-829.

Tanaka S and Itozaki H. (1988). High J_c Superconducting Single Crystalline HoBaCuO Thin Films by Sputtering. Jpn. J. Appl. Phys. **27**, 622-624.

Tarascon JM, McKinnon WR, Greene LH, Hull GW, Bagley BG, and Vogel VG. (1987).Processing and Superconducting Properties of Perovskite Oxides. Adv. Ceram. Materials **2**, 498-505.

Terada N, Ihara H, Jo M, Hirabayashi M, Kimura Y, Matsutani K, Hirata K, Ohno E, Sugise R, and Kawashima F. (1988). Sputter Synthesis of $YBa_2Cu_3O_y$ as Deposited Superconducting Thin Films from Stoichiometric Target: A Mechanism of Compositional Deviation and its Control. Jap. J. Appl. Phys. **27**, L639-642.

Terasaski I, Nakayama Y, Uchinokura K, Maeda A, Hasegawa T, and Tanaka S. (1988). Superconducting Films of $YBa_2Cu_3O_x$ and Bi-Sr-Ca-Cu-O Fabricated by Electron Beam Deposition with a Single Source. Jpn. J. Appl. Phys. **27**, L1480-1483.

Terashima T, Ijima K, Yamamo K, Bando Y, and Mazaki H. (1988). Single Crystal $YBa_2Cu_3O_{7-x}$ Thin Films by Activated Reactive Evaporation. Jap. J. Appl. Phys. **27**, L91- 93.

Thornton JA. (1988). Physical Vapor Deposition. In "Semiconductor Materials and Process Technology Handbook", G. E. McGuire (Ed.), Noyes Publications, Park Ridge, NJ, 329- 454.

Tietz LA, De Cooman BC, Carter CB, Lthrop DK, Russek SE, and Burhman J. (1988). Structure of Superconducting Thin Films of $YBa_2Cu_3O_{7-x}$ Grown on $SrTiO_3$ and Cubic Zirconia. J. Electron Microsc. Techn. **8**, 263-272.

Tsaur BY, Dilorio MS, and Strauss AJ. (1987). Preparation of Superconducting $YBa_2Cu_3O_x$ Thin Films by Oxygen Annealing of Multilayer Metal Films. Appl. Phys. Lett. **51**, 858-860.

Venkatesan T, Wu XD, Inam A, Jeon Y, Croft M, Chase EW, Chang CC, Wachtman JB, Odom RW, di Brozolo FR, and Magee CA. (1988a). Nature of the Pulsed Laser Process for the Deposition of High T_c Superconducting Thin Films. Appl. Phys. Lett. **53**, 1431-1433.

Venkatesan T, Wu WD, Inam A, and Wachtman JB. (1988b). Observation of Two Distinct Components during Pulsed Laser Deposition of High T_c Superconducting Films. Appl. Phys. Lett. **52**, 1193-1195.

Venkatesan T, Chang CC, Dijkkamp D, Ogale SB, and Chase EW. (1988c). Substrate Effects on the Properties of Y-Ba-Cu-O Superconductor Films Prepared by Laser Deposition. J. Appl. Phys. **63**, 4591-4598.

Venkatesan T, Wu XD, Dutta B, Inam A, Hedge MS, Hwang DM, Chang CC, Nazar L, and Wilkens B. (1989). High Temperature Superconductivity in Ultra Thin Films of $YBa_2Cu_3O_{7-x}$. Appl. Phys. Lett. **54**, 581-583.

Wang WN, Lu HB, Lin WJ, Yao PC, Hsu HE, Tai MF, and Ku HC.(1988). Formation of High T_c $YBa_2Cu_3O_{7-x}$ Films on Y_2BaCuO_5 Substrate. Jpn. J. Appl. Phys. **27**, L1268-1270.

Wasa K, Kitabatake M, Azachi H, Setsune K, and Hirochi H. (1988). Superconducting Y-Ba-Cu-O and Er-Ba-Cu-O Thin Films Prepared by Sputtering/Deposition.

Amer. Inst. of Phys. Conf. Proc. "Thin Film Processing and Characterization of High Temperature Superconductors", Harper JME, Colton RJ, and Feldman LC (Eds.), No**165**, p. 38-49.

Webb C, Weng SL, Eckstein JN, Missert N, Char K, Schlom DG, Hellman ES, Beasley MR, Kapitulnik A, and Harris JS, Jr. (1987). Growth of High T_c Superconducting Films Using Molecular Beam Epitaxy Technology. Appl. Phys. Lett. **51**, 1191-1193.

Weimer WA. (1988). Plasma Emission from Laser Ablation of the High Temperature Superconductor $YBa_2Cu_3O_7$. Appl. Phys. Lett. **52**, 2171-2173.

Whener G, Kim YH, Kim DH, and Goldman AM. (1988). Sputter-Deposition of $YBa_2Cu_3O_{7-x}$ Films Using a Hemispherical Target in a Hg Vapor Triode Plasma. Appl. Phys. Lett. **52**, 1187-1189.

Wiesmann H, Chen DH, Sabatini RL, Hurst J, Ochab J, Ruckman MW. (1989). Effect of stoichiometry and Post-Annealing Conditions on Magnetron Sputtered Films of $YBa_2Cu_3O_7$ on Cubic Zirconia. J. Appl. Phys. **65**, 1644-1647.

Witanachchi S, Kwok HS, Wang XW, and Shaw DT. (1988). Deposition of Superconducting Y-Ba-Cu-O Films at 400 °C without Post-Deposition Annealing. Appl. Phys. Lett. **53**, 234-236.

Witanachchi S, Patel S, Kwok HS, and Shaw DT. (1989). As Deposited Y-Ba-Cu-O Superconducting Films on Silicon. Appl. Phys. Lett. **54**, 578-580.

Wu MK, Ashburn LR, Torng CJ, Hor PH, Meng RL, Gao L, Huang ZJ, Wang YQ, and Chu CW. (1987a). Superconductivity at 93 K in a New Mixed-Phase Y-Ba-Cu-O Compound System at Ambient Pressure. Phys. Rev. Lett. **58**, 908-910.

Wu MK, Dijkkamp D, Ogale SB, Inam A, Chase EW, Micelli PF, Chang CC, Tarascon JM, and Venkatesan T. (1987b). Epitaxial Ordering of Oxide Superconductor Thin Films on (100) $SrTiO_3$ Prepared by Pulsed Laser Evaporation. Appl. Phys. Lett. **51**, 861-863.

Wu MK, Inam A, Hedge MS, Wilkens B, Chang CC, Hwang DM, Nazar L, Venkatesan T, Miura S, Matsubara S, Miyasaka Y, and Shohata N. (1989). High Critical Currents in Epitaxial $YBa_2Cu_3O_{7-x}$ Thin Films on Si with Buffer Layers. Appl. Phys. Lett. **54**, 754-756.

Yee DS, Gambino RJ, Chisholm MF, Cuomo JJ, Madakson PB, and Karasinski J. (1987). Critical Current and Texture Relationships in $YBa_2Cu_3O_7$ Thin Films. Amer. Inst. of Phys. Conf. Proc. "Thin Film Processing and Characterization of High Temperature Superconductors", Harper JME, Colton RJ, and Feldman LC (Eds.), No **165**, 132-140.

Ying QY, Shaw DT, and Kwok HS. (1988). Spectroscopic Study of Plasma-Assisted Laser Deposition of Y-Ba-Cu-O. Appl.Phys. Lett. **53**, 1762-1764.

Zheng JP, Huang ZQ, Shaw DT, and Kwok HS. (1989a). Generation of High- Energy Atomic Beams in Laser-Superconducting Target Interactions. Appl. Phys. Lett. **54**, 280-282.

Zheng JP, Ying QY, Witanachchi S, Huang ZQ, Shaw DT, Kwok HS. (1989b). Role of the Oxygen Atomic Beam in Low-Temperature Growth of Superconducting Films by Laser Deposition. Appl. Phys. Lett. **54**, 954-956.