

HTS FILM GROWTH

Thin films of superconductors are primarily of interest for electronics applications. High-performance superconducting thin films are essential, for example, for high-frequency passive devices and Josephson junction circuits. Thin films are also important for fundamental studies of superconducting materials, where specially designed experiments can take advantage of the thin layer geometry and the capability of layering various combinations of materials, as well as lithographically defining fine features in them. Additionally, there is currently growing interest in using thin film deposition technology for deposition of thick films on polycrystalline substrates for power applications.

In the decade since the discovery of high-temperature superconductivity (*HTS*) in cuprate compounds, thin film materials have played an important role in the evolution of this field. The discovery of HTS has led to a rapid development of many different thin film deposition techniques. HTS thin films are now routinely made in hundreds of laboratories around the world, and thin film research is actively pursued in areas such as new superconducting materials and epitaxial oxide heterostructures. More recently, advances in deposition processes have brought about the synthesis of larger-area HTS films, making fabrication less expensive and allowing for high-throughput manufacturing of single-superconducting-layer films.

In this article, we review the physical vapor deposition (*PVD*) techniques most frequently used for HTS thin film synthesis. Chemical vapor deposition techniques are reviewed in another article of this encyclopedia. Here, we review only the methods and issues that are relevant for film deposition. This does not cover the details of the film growth processes, nor the physical properties of HTS films and their applications. The reader is referred to other references for a more complete discussion of HTS thin films and their applications (1,2).

Materials

The HTS material of choice for applications is still $\text{YBa}_2\text{Cu}_3\text{O}_7$ (*YBCO*), the first cuprate discovered to superconduct above 77 K. There are several compelling reasons why this material is still the most suitable for many of the applications. Some of the fundamental ones are its smaller conduction anisotropy, higher superconducting critical currents in a magnetic field, and greater chemical stability than in other HTS compounds. However, the most important reason is the ease of fabricating high-quality, single-phase YBCO thin films.

In this review, YBCO will be considered the canonical high- T_c superconductor, and the discussion will be limited to this example, partly for reasons of conciseness and partly because of the prominence of this compound in the HTS community. Additionally, unless otherwise mentioned, one is generally considering growth of *c*-axis-oriented films, i.e. where the CuO_2 layers are parallel to the substrate.

Table 1 reviews the HTS compounds and methods used to date to prepare these thin films. For a review of materials, we refer the reader to Refs. 2 and 3. There has been a substantial effort related to Bi–Sr–Ca–Cu–O thin films (2212 and 2223 phases) by a variety of techniques, particularly in Japan. Some industrial work in the US has focused also on Tl–Ba–Ca–Cu–O (mostly 2212), primarily for passive electronics applications. One of the obvious reasons for looking at these other compounds is their higher critical temperatures. Nevertheless,

2 HTS FILM GROWTH

Table 1. HTS Materials Systems, Methods Used to Fabricate Thin Films, and Applications of the Thin Films

Material	T_c (K)	Thin Film Deposition Technique	Applications
Y(R)BaCuO 123	85–95	In situ: sputtering, PLD, evaporation, MOCVD; ex situ	RF devices, Josephson junctions
BiSrCaCuO 2201, 2212, 2223	10–115	In situ: sputtering, PLD, evaporation	Josephson junctions
TlBaCaCuO 1201, 1212, 1223, 2201, 2212, 2223	20–125	1212: In situ sputtering; ex situ	RF devices
HgBaCaCuO 1201, 1212, 1223	95–133	Ex situ	
LaSr(Ba)CuO	20–40	In situ	
NdCeCuO	20–30	In situ	

the advantages of YBCO have been hard to surpass, particularly at temperatures below 65 K. Substantial thin-film work has also been devoted to La–Sr–Cu–O, Nd–Ce–Cu–O, Hg–Ba–Ca–Cu–O, and infinite-layer compounds, mostly driven by academic interest in basic properties of these HTS materials.

Thermodynamic Issues

Film growth is inherently a nonequilibrium process. Nevertheless, thermodynamic stability is important as a driving force for the reactions taking place during growth. HTS compounds possess large unit cells which can have additional complications, such as a wealth of metal-atom defects and oxygen nonstoichiometries. These complex structures require temperatures for formation close to their melting points, typically $(0.8–0.9)T_m$, much higher than is usual for growth of epitaxial metals and semiconductors. The intricacies of film growth and the thermodynamics of phases produced are certainly not sufficiently well understood at present. Below, we summarize some of the key thermodynamic issues as they are currently accepted.

Oxygen Stability. HTS compounds are oxides and, as such, require the presence of oxygen during synthesis. Although it is technically possible to deliver oxygen through the substrate, in practice, oxygen is delivered as a gas impinging on the growth surface together with the cation species. Figure 1 shows the pressure–temperature thermodynamic stability diagram for the bulk YBCO compound. One can see from the diagram that a certain minimum pressure must be maintained for the stability of YBCO. Below that oxygen pressure, depicted by the line labeled d_1 , the YBCO compound is not stable and will decompose. For the typical temperatures during film formation, this translates into a minimum oxygen pressure of about 100 mPa (1 mtorr). At higher oxygen pressures, there is another decomposition line for YBCO, labeled d_2 , usually not reached during in situ growth of thin films. During cooldown of films to room temperature, this second decomposition is usually not observed because it is strongly limited by diffusion kinetics. However, the stability diagram also implies that the YBCO compound is metastable at room temperature and pressure. In fact, most HTS compounds are believed not to be thermodynamically stable at lower temperatures. References 4 and 5 have a more detailed discussion of the YBCO stability lines. Hammond and Bormann (6) argued that growth of thin films is optimal close to the high-temperature thermodynamic decomposition line of the compound.

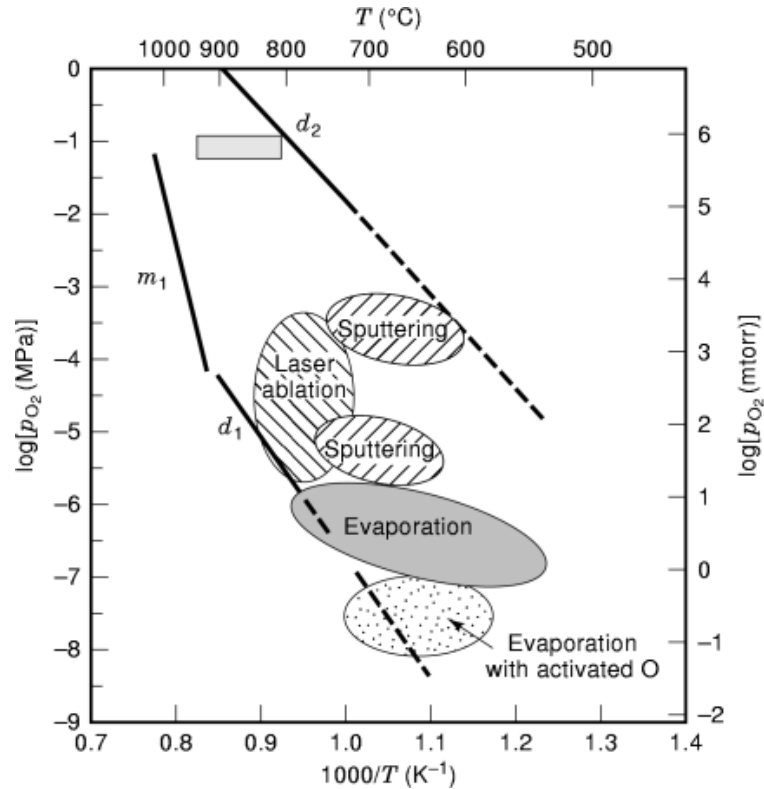


Fig. 1. Thermodynamic stability diagram for YBCO in oxygen pressure and temperature. The shaded elliptical areas indicate regimes where in situ film growth for YBCO has been reported successful. The rectangles show ex situ film growth regimes.

In fact, the empirical data confirm this, as can be seen also in Fig. 1, where successful film growth regions are denoted. For processes that possess a more reactive form of oxygen, such as atomic oxygen or ozone, the equivalent decomposition line is shifted compared with that in Fig. 1. Such activated oxygen species have been proven helpful for growth of YBCO when the total pressure is lower than about 1 Pa (10 mtorr).

Compositional Phase Diagram. The HTS compounds contain typically three to five different metal species in addition to oxygen. Some of these materials are line compounds (and this is presumed to be the case for YBCO) and, as such, do not accept a solid solution of atoms in their chemical formula. This means that one will always be synthesizing a number of phases in addition to the desired HTS material. For YBCO, the Gibbs phase rule implies two other compounds as impurity phases. Figure 2 shows the present understanding of the ternary phase diagram for Y–Ba–Cu oxides at the low oxygen pressures relevant for in situ thin film growth (7,8). The corners of the triangles define the phases which will be present for any composition in that triangle.

There are some caveats to the description given above. First of all, as already stated, film growth is not an equilibrium process, and therefore metastable phases could be formed during synthesis. Secondly, the HTS material that is formed during film growth may not be, and probably is not, exactly like the bulk material. This has now been well documented in the literature for YBCO films. In fact, it is also fairly well established that YBCO film growth does not match exactly the thermodynamic phase diagram shown in Fig. 2. In particular, the Y_2BaCuO_5 phase has not been observed in in situ grown films. On the other hand, CuO and Y_2O_3 second

4 HTS FILM GROWTH

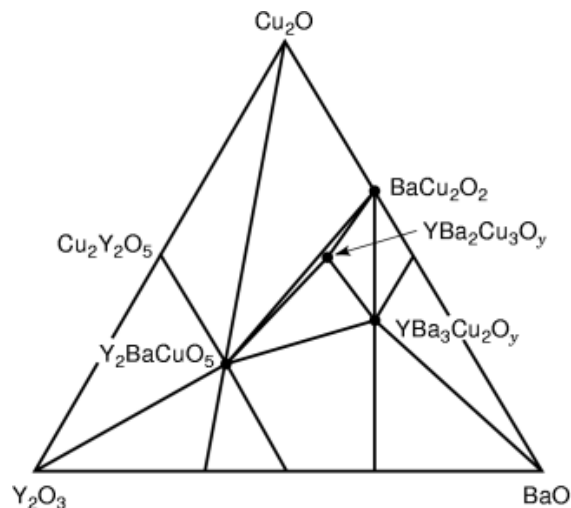


Fig. 2. Thermodynamic ternary phase diagram for Y–Ba–Cu oxides at temperatures below 850°C and oxygen pressures below one atmosphere.

phases are commonly observed in YBCO films prepared close to 1:2:3 stoichiometry and are not predicted by the phase diagram.

Epitaxy

Due to the significant anisotropy of the HTS materials, the easy direction for electrical current flow is in the ab plane, along the Cu–O₂ planes. For devices which require current to flow parallel to the substrate, the growth direction of the HTS films has to be in the c -axis direction. In order to achieve c -axis-oriented growth, good epitaxial growth of all grains is necessary. Furthermore, a high-angle, in-plane grain boundary of two c -axis-oriented grains has been found to behave as a superconducting weak link. This implies that one needs to align all grains in the plane of the substrate as well as out of the plane. The requirements of in-plane epitaxy are very well illustrated in the case of yttria-stabilized zirconia (YSZ) substrates where the YBCO films grow in the c direction, but the c axis grains can have two major different orientation in the ab plane, 45° apart (15). In the case of applications which require the current flow to be perpendicular to the substrate, a -axis growth has been implemented. Many multilayer Josephson devices have been tried in this way. a -axis growth is typically initiated with a lower substrate temperature, which in turn reduces the mobility of ions necessary for the c -axis growth. Due to the lower growth temperature, films are formed which are structurally less perfect. To overcome this problem, many workers have used a technique of starting growth at a lower temperature for a -axis nucleation, making a template, and then raising the temperature for the remainder of film deposition (16).

Substrates. The most frequently used substrate for fundamental research is SrTiO₃ because of its good thermal and lattice constant match with most HTS materials. However, high dielectric loss, small wafer size, and high cost of SrTiO₃ render it unfavorable for technological applications. LaAlO₃ has emerged as an alternative to SrTiO₃ as a low-loss perovskite substrate, although its critical dielectric properties are not under complete control. MgO substrates, on the other hand, have an even lower loss for microwave applications. However, the reproducibility of the MgO surface quality has been a problem in the earlier days, but more recently, the surface quality has improved. For applications where very low loss is required, MgO is the best HTS substrate at present. MgO and LaAlO₃ are commercially available in wafer sizes larger than 5 cm (2 in.).

Table 2. Substrates and Buffer Layer for HTS Thin Films

Substrate	Orientation	Buffer Layer
SrTiO ₃	(100)	none CeO ₂
LaAlO ₃	(100) pseudocubic	CeO ₂ none
MgO	(100)	none SrTiO ₃
YSZ	(100)	CeO ₂ Y ₂ O ₃
Al ₂ O ₃	(1102)	CeO ₂ MgO
Si	(100)	YSZ/Y ₂ O ₃ YSZ/CeO ₂

More conventional substrates such as Si and sapphire have been used and found to be incompatible with thick HTS thin films, mainly due to microcracking in the HTS films resulting from the thermal expansion mismatch between the substrates and the HTS materials. The maximum thickness of YBCO one can grow without significant microcracking is about 50 nm on Si and about 600 nm on sapphire. Table 2 shows a list of substrates most commonly used today for growth of HTS films. References 17 and 18 have a more extensive discussion of HTS compatible substrates and buffer layers.

In most cases, excellent epitaxial alignment can be achieved by depositing oxide buffer layers, such as CeO₂, before HTS growth. The CeO₂ buffer layer has been found to suppress the unwanted *a*-axis nucleation for the *c*-axis growth on substrates such as SrTiO₃ and LaAlO₃. On substrates such as YSZ and *r*-plane sapphire, the CeO₂ buffer layer promotes in-plane alignment of each *c*-axis grain, thereby eliminating potential high-angle grain boundaries. In fact, by using an appropriate buffer layer and a seed layer, one can create a process to produce 45°-angle grain boundaries in a controlled fashion. On Si substrates, the YSZ buffer layer was found to grow epitaxially and to be very effective in preventing chemical reaction between HTS materials and Si.

Ion-Beam-Assisted Deposition. Recently, a new technique, ion-beam-assisted deposition (*IBAD*), has been implemented to grow HTS layers on polycrystalline substrates. By bombarding the growing film surface with an ion beam incident at a specific angle to the substrate, one is able to achieve partial in-plane crystalline alignment of the deposited material where the substrate has none. Iijima et al. (19) first utilized this technique to grow in-plane textured zirconia buffer layers on substrates made of polycrystalline Ni-based alloys. YBCO was then deposited by PLD. Due to the absence of high-angle grain boundaries in YBCO, the critical currents attained are much higher than without the IBAD process. Other groups, including the one at Los Alamos National Laboratory, has followed on this work and achieved critical currents over 10⁶ A/cm² at 77 K (20). More recently a group at Stanford University has demonstrated very good IBAD results with 10 nm thick MgO films (21). While more development is needed to establish whether the IBAD process is a viable one for large-scale applications, it certainly opens up a whole new range of substrate materials for HTS film growth.

Film Growth Methods

Most of the methods currently employed for fabrication of HTS thin films involve formation of the cuprate crystal structure during film deposition. These are usually called *in situ* processes, and they will comprise most cases covered in this review. Chemical vapor deposition processes, which are also *in situ* growth, are covered in another chapter of this volume. Historically, the processes that were developed first, required a postdeposition anneal, or simply postanneal, in order to crystallize the material. Such methods are now less frequently utilized, since they are not well suited for fabrication of multilayer structures and are thus technologically

6 HTS FILM GROWTH

more limiting. However, they are still used for compounds such as TlBaCaCuO or HgBaCaCuO , where the in situ processes are often not practical due to the required high vapor pressures of Hg and Tl. Finally, there are other processes such as sol-gel, plasma spray deposition, and liquid phase epitaxy that are generally used for fabrication of thick films (thicker than $1\ \mu\text{m}$); these also will not be covered in this brief review.

Postanneal Growth Methods. In the post-anneal, or ex situ, growth process, the metallic elements are deposited on a substrate in the correct composition as an amorphous or multilayer film, usually in compound form with oxygen and possibly fluorine. Subsequent annealing in air or oxygen at a high temperature, typically $\geq 850\ ^\circ\text{C}$ for YBCO, forms an epitaxial film of the desired HTS phase (9). A very commonly used postanneal method for growth of YBCO films is achieved by using BaF_2 in the precursor film. Water is then required in the annealing step in order to eliminate the fluorine and start the HTS growth process. Since the critical growth step takes place separately from deposition, the actual technique used to deposit the layers is of secondary importance. Sputtering and evaporation are typically used.

Ex situ methods have initially focused on synthesis under atmospheric oxygen pressure and correspondingly high temperatures. This region of phase space is depicted in Fig. 1 with the rectangle in the upper left corner. Later work has shown that lower-temperature ex situ growth can also be achieved if the oxygen pressure is reduced at the same time (see also the lower rectangle in Fig. 1). Such films grown under lower oxygen pressures were observed to have properties closer to the in situ grown films (10,11).

In situ Growth Methods. Dominant methods in use today for physical vapor deposition of HTS are sputtering and laser ablation (also referred to as pulsed laser deposition, or *PLD*). Both of these methods are most commonly done from a single target and as such, became rather popular mostly because they are relatively simple to implement and fairly reproducible in the films they produce. In addition, targets for PLD are relatively inexpensive and easy to fabricate, and hence, the technique is well suited for investigation of many different materials. Less widespread today, but currently growing in popularity, are coevaporation and molecular beam epitaxy. After the initial slow start in contending with a sufficiently oxidizing environment in high vacuum, evaporation methods have now emerged as an established way to grow high-quality HTS films.

The following is a list of in situ physical vapor deposition techniques used for deposition of HTS compounds, which will be covered in this review:

(1) Sputtering

- On-axis magnetron
- Off-axis magnetron
- Inverted cylindrical magnetron
- Ion-beam sputtering

(2) Laser ablation

- On-axis
- Off-axis
- Laser-MBE

(3) Evaporation

- Flash evaporation
- Reactive coevaporation
- Reactive-MBE

For more discussion on various PVD techniques, we also refer the reader to Refs. 12,13, and 14.

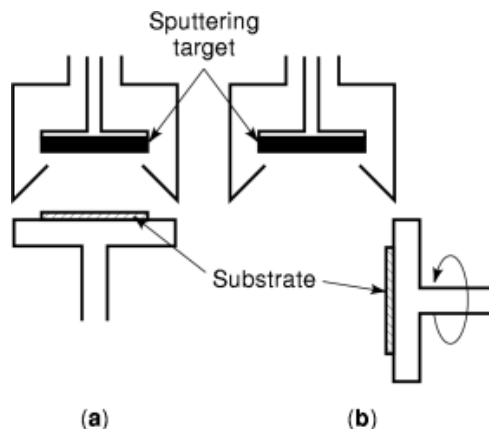


Fig. 3. Schematic for the (a) on-axis and (b) off-axis sputter deposition.

Sputtering

Sputtering is a very commonly used technique for metal deposition in semiconductor and magnetic storage industries. As such, it was applied early on to HTS materials. The first event of significance was the use of a single composite target, which became commonplace for HTS materials because of the inherent difficulty of reproducing the metal-atom stoichiometry. The major complication compared to more conventional sputtering of metals is the energetic negative-ion (oxygen) bombardment of the substrate, due to the ionic nature of the oxide target. This causes resputtering and degradation of the sample. This has been recognized even before the advent of HTS and has been fully investigated by Rosnagel and Cuomo (22). Two types of solutions had emerged: (1) using a higher gas pressure in order to thermalize the energetic species (23), and (2) off-axis sputtering, where one eliminates the high-energy particles coming directly from the target (24,25). Figure 3 shows the schematic of the two processes. Other variations include on-axis unbalanced-magnetron sputtering (26) and inverted cylindrical magnetron (*ICM*) sputtering (27).

The energies of ejected atoms from the sputtered targets are in the range of tens of electron volts, and they get scattered by the background Ar and O₂ gas. The angular distribution of each cation species is different, and the *sweet spot* for the proper cation composition is relatively small. In order to cover a 5-cm (2-in.) wafer uniformly from a single 5-cm target in an off-axis geometry, one has to resort to some sort of scanning method, such as rotation of the wafer. The deposition rate is very low, not only because the deposition rate for oxides is much lower than for metals, but also because of the off-axis geometry. It takes several hours to deposit a few hundred nanometers of film. Larger targets and a number of sputter guns depositing simultaneously have been used at several laboratories to increase the deposition rate. When all the deposition conditions are optimum, sputtering has demonstrated a capability to produce YBCO films of excellent crystallinity and surface condition. However, the deposition conditions have to be changed as the targets erode, because the changing target surface geometry results in a different plasma distribution. In addition, the substrate heating method for off-axis sputtering is not as simple as in the case of the off-axis laser ablation or evaporation which will be described later.

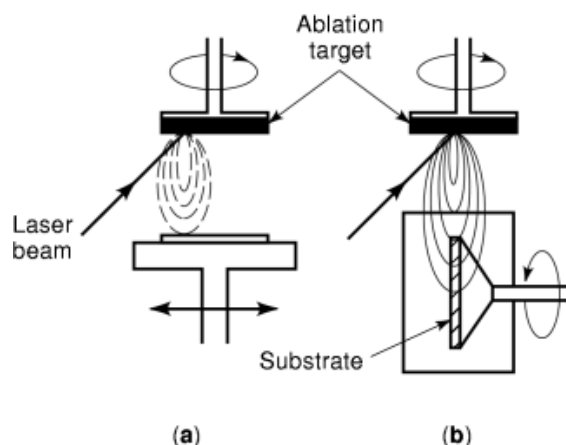


Fig. 4. Schematic for the (a) on-axis and (b) off-axis laser ablation processes.

Laser Ablation

Laser ablation, or pulsed-laser deposition (*PLD*), is a relatively new technique that gained much popularity because it is ideally suited for deposition at a high oxygen pressure. The relative ease of this technique in depositing multicomponent oxides (and nitrides) has made it especially effective in exploring new materials for HTS electronics, such as epitaxial dielectrics or barrier layers. A short-wavelength (170 to 260 nm) excimer laser is focused onto a rotating target of the material to be deposited. Under the energy of the laser beam (0.1 to 2 J per pulse), the matter emitted from the target forms a plume that carries it to the substrate at supersonic velocities. In general, a higher gas pressure is required during laser ablation, due to the very high energy of the vaporized material from the surface of the target. The laser plume glows brightly from the target, and deposition is usually done near the end of the plume, about 5 cm away; see Fig. 4. Again, as in the case of sputtering, the various species scatter differently, and therefore the sweet spot of the deposition process is relatively small, usually one to two centimeters, depending on the geometry. The deposition rate per laser pulse ranges from a fraction of an angstrom to a few angstroms. The technique was found to be fairly reproducible from the early days and has been used extensively for research and development purposes during the past ten years. Even though other techniques are potentially more manufacture-friendly, laser ablation is still very actively used for prototyping devices made up of several complex materials, such as superconductors, ferroelectric oxides, and magnetic oxides.

A particular problem associated with PLD is the deposition of micron-size droplets, so-called *boulders*, on the grown film. These particles originate at the target and are emitted from the action of the laser pulse. A variety of procedures have been utilized to reduce this problem, so that the boulder density can be very low in the best films. Such procedures include target preparation (such as frequent polishing), defocusing the laser spot, mechanically chopping the plume, and spatially filtering the beam.

Although PLD can produce high deposition rates (up to tens of nanometers per second), the area on which one deposits is small. A straightforward way to increase the deposition area is to scan wafers over the plume either by moving the substrate vertically and horizontally or by rotating the substrate. This method has been tried in several laboratories and is still pursued. Another scheme utilizes a rotating cylindrical target with a linear laser profile to obtain larger deposition areas.

Another major difficulty of these techniques is uniform heating of large wafers. Most of the heating methods for small-area laser ablation have been to mount a substrate on a heated metal surface with silver

paste, which is difficult to extend to larger sizes. In order to overcome this difficulty of heating a large wafer, an off-axis laser ablation technique has been developed; see Fig. 4(b). A large wafer (5 to 8 cm) can be mounted parallel to the direction of the plume inside a relatively simple blackbodylike heater. The deposition takes place when the atoms collide with the background pressure and are scattered to the surface of the wafer. By rotating the wafer and selecting an appropriate pressure for the geometry, a fairly uniform deposition was achieved over 5 cm wafers. This technique allows for simultaneous deposition on both surfaces of the wafer, which is an important benefit for microwave applications requiring a ground plane. A drawback of this technique is its low deposition rate because of the off-axis geometry. Typical conditions for deposition of a 5 cm wafer resulted in a deposition rate about a factor of 10 lower than for the on-axis deposition.

By using laser fluence just enough to evaporate a few atomic layers of the target in a low-oxygen environment (less than 10^{-2} Pa $\approx 10^{-4}$ torr) and at the same time using a sequence of metal or metal oxide targets, one can obtain a process similar to molecular beam epitaxy (*MBE*) by evaporation, here called laser MBE. Some in situ diagnostic tools can then be used to characterize the growth of the materials. This technique has mainly been used to grow artificially layered superconducting materials, such as the infinite-layered superconductor (28,29).

Evaporation and Molecular Beam Epitaxy

Deposition of HTS thin films by evaporation follows a tradition of such deposition of metal films. The added complexity here is the required partial pressure of oxygen during growth. One can distinguish several variations in the evaporation approaches: flash evaporation, reactive coevaporation of metals, and sequential deposition by MBE. Except for the first process, these evaporation techniques utilize individual metallic sources. However, in attempting to control individual sources, two difficulties arise. One is the need for very fine control of individual sources, including development of species-specific sensors. The second is the need to work at a low enough pressure to minimize beam scattering and at the same time achieve the highly oxidizing thermodynamic conditions required for the growth of these compounds. For an in situ process, one is confined to work at a pressure of molecular oxygen above 100 mPa (1 mtorr) or to use a more reactive form of oxygen supply than molecular oxygen.

Flash Evaporation. The simplest approach to evaporation of HTS materials is to evaporate the compound in small batches, i.e. in flashes of evaporant material. Since the material does not melt congruently, it is not possible to establish a continuously constant rate of metal fluxes, but for short enough intervals one can average out the compositional variations. Usually, the evaporant material is a powder of YBCO located in a feed mechanism that drops small quantities onto an evaporation source (30). In most cases, the films require a postannealing treatment to oxidize the film sufficiently, since the fast deposition does not allow for sufficient incorporation of oxygen. This method is at present less significant.

Reactive Coevaporation. Historically, the first attempts to make films by evaporation utilized a high molecular oxygen pressure. The problems associated with a high background oxygen pressure are rate control of the individual species and the degradation of the sources. In order to circumvent this difficulty, several approaches were taken. One was to accommodate a high differential pressure between the sources and the sample by introduction of nozzles in close proximity to the sample. Another method is to utilize a more reactive species for oxygen incorporation, such as atomic oxygen or ozone.

The evaporation technique allows one to tune the composition of the film by adjusting the relative rates of the sources. Several groups have worked over the past years on developing process control for coevaporation and studying YBCO film properties as a function of metal atom composition. Figure 5 shows SEM micrographs of films with various metal compositions. The general finding is that films that are grown slightly Y- and Cu-rich have better performance than films with exactly 1:2:3 stoichiometry. This is true for a majority of in situ techniques and not just evaporation. The reasons for this are still not completely clear—in particular,

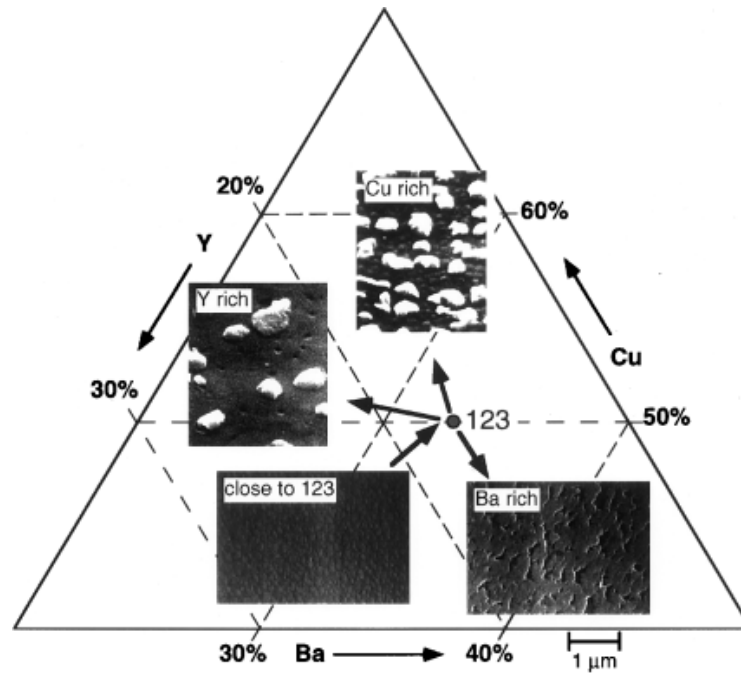


Fig. 5. Morphology of YBCO films as a function of their composition during reactive coevaporation.

whether it is a materials issue or a process control issue. It is known that superconducting properties of films degrade significantly as one goes into the Ba-rich composition. It is possible that process fluctuations around the desired metal-atom stoichiometry are responsible for degradation of films close to 1:2:3 composition.

Probably the most technologically significant advance in HTS thin film evaporation has been the large-area heater developed for coevaporation by the group of H. Kinder at the Technical University of Munich (Germany) and depicted in Fig. 6. They used a blackbody-type rotating disk heater, similar to the one used by others in PLD deposition, but they added an *oxidation pocket* (31). This heater has a narrow slit that allows for a differential pressure between the oxidation pocket and the rest of the chamber of about 1000:1. The deposition and the oxidation processes are therefore separated, and a low pressure in the chamber improves the stability of thermal evaporation sources. Uniform YBCO films were grown on wafers up to 20 cm in diameter using this technique. More importantly, this method is significantly more cost-effective and has higher throughput than any of the other PVD processes.

Molecular Beam Epitaxy. In general, one can distinguish between reactive molecular beam epitaxy (*MBE*) approaches to HTS film deposition and mere reactive evaporation by the lower background pressure of the former technique. Another difference is that MBE deposition is usually done sequentially rather than simultaneously. Typically, MBE systems have multiple sources with individual shutters, as well as some in situ monitoring tools; see Fig. 7. Reference 32 has a thorough discussion of relevant issues in reactive MBE of HTS films. The work by a number of groups in this field has focused on careful atomic layering to produce very smooth films, as well as customized growth of new materials and heterostructures containing these phases. The reactive MBE technique also lends itself to careful control of chemical doping of these materials, an issue that is very important for the superconducting properties of the cuprates.

In situ Monitoring and Diagnostics. Evaporation and, especially, MBE, with their inherent low background pressure, lend themselves well to vacuum techniques for in situ deposition monitoring and film

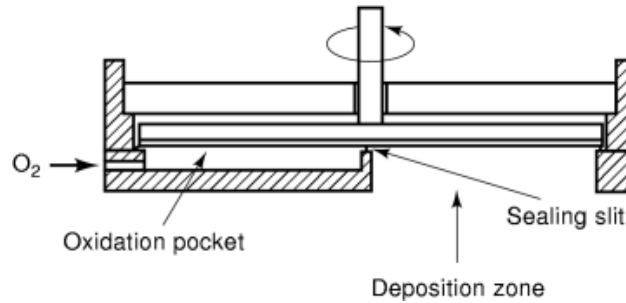


Fig. 6. Schematic of the heater for large-area HTS deposition by evaporation.

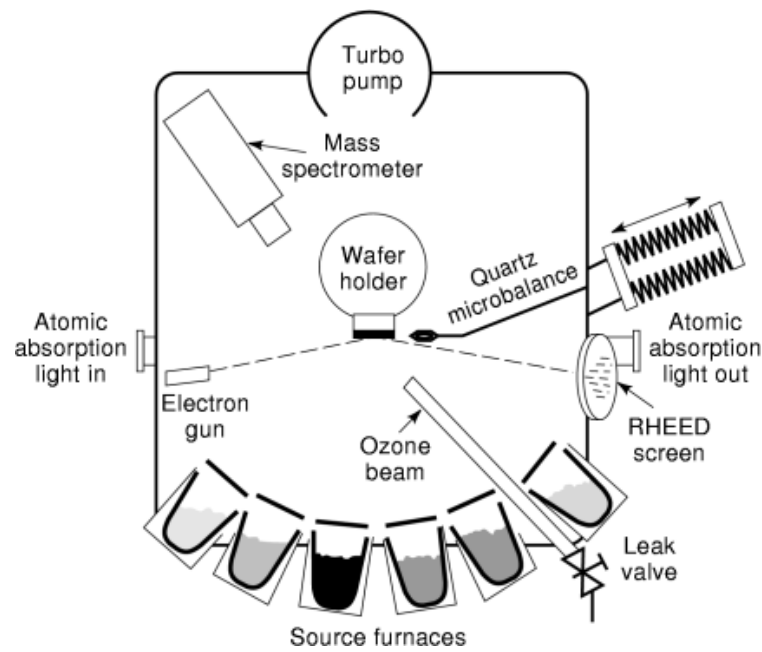


Fig. 7. Schematic for the reactive MBE process used in HTS film growth.

diagnostic tools such as reflection high-energy electron diffraction (*RHEED*). *RHEED* has been shown to be particularly helpful in controlling deposition of Bi–Sr–Ca–Cu–O films, where the growth occurs in blocks of subunit cells, but where many similar phases are possible. *RHEED* has been less helpful to date in the growth of YBCO, which occurs in blocks of unit cells and where intergrowths are more difficult to tailor due to the higher stability of the primary phase. Terashima and coworkers (33) have shown that growth of YBCO can exhibit oscillations in the *RHEED* pattern commensurate with unit cell deposition, suggesting that growth proceeds in a unit-cell-by-unit-cell fashion, rather than in smaller building blocks. More recently, *RHEED* has also been extended to high-pressure processes such as PLD (34).

Another area of technological development has been in the use of optical absorption techniques for measurement and control of atomic fluxes. Both hollow-cathode lamp systems (35) and tunable diode lasers (36) have been used to monitor fluxes in situ in close proximity to the substrate. Such monitoring of individual fluxes is a prerequisite for careful control of HTS growth.

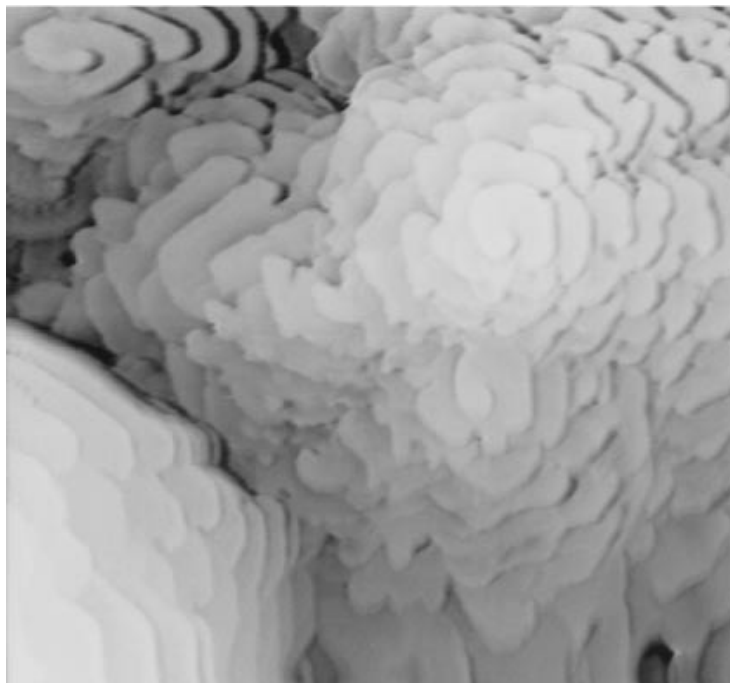


Fig. 8. An STM image of a laser ablated YBCO film, showing spiral growth structures. Image courtesy of Prof. Darrell Schlom.

Concluding Remarks

In spite of a wealth of research, growth of cuprate films has remained a complicated matter. This is due to the materials' rather complex multicomponent crystal structures. They are prone to a variety of defects and growth morphologies. Much work still remains to be done until films are better understood and more reproducible.

As already described, HTS films are now routinely made with out-of-plane as well as in-plane alignment on single-crystalline substrates. Aligned films are still not routine on polycrystalline substrates, but there has been progress in this area as well. This has been manifested in high critical currents in films, particularly for YBCO. Typical critical currents in good quality YBCO films are over 2×10^6 A/cm² at 77 K and above 10^7 A/cm² at low temperatures. There has been much work in characterizing defect structures, but a good understanding of their influence on physical properties is still lacking. One growth structure that seems to be nearly ubiquitous in YBCO films is the spiral, which forms during growth and at the core of which is a screw dislocation (36). Figure 8 shows a scanning tunneling microscopy (STM) image of a surface of a YBCO film with a spiral. Steps in this image have a height of one unit cell of YBCO. Such spirals have been identified as contributing to pinning of vortices, important for high critical currents.

Maximally oxygen-doped YBCO bulk materials, made at higher temperatures than thin films, have a superconducting transition temperature of 92 K and a resistivity of $35 \mu\Omega \cdot \text{cm}$ at 100 K. Although having nominally the same crystal structure as the bulk material, YBCO films often have different electronic properties. For example, lower T_c (85 to 90 K) and expanded c -axis lattice constants (1.170 to 1.172 nm) are frequently found in thin films. Additionally, flux-pinning centers appear to be highly dispersed in in situ grown films of YBCO, although the structural origin of these centers has not yet been identified. It is important to have a

close feedback loop between film deposition and structural and electrical characterization in order to further improve HTS films.

Technology for deposition and monitoring of HTS thin films has developed significantly over the past decade. At the same time, the materials understanding of film nucleation, growth, and oxide interfaces has started to unfold. Together, these developments in the future will bring new capabilities for HTS film growth.

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14 HTS FILM GROWTH

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