

## Growth of cuprate high temperature superconductor thin films

H-U Habermeier

MPI-FKF Heisenbergstr.1 D 70569 Stuttgart, Germany

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### Abstract

This paper reviews briefly the development of physical vapour deposition based HTS thin film preparation technologies to today's state-of-the-art methods. It covers the main trends of in-situ process and growth control. The current activities to fabricate tapes for power applications as well as to tailor interfaces in cuprate are described. Some future trends in HTS thin film research, both for science as well as application driven activities are outlined.

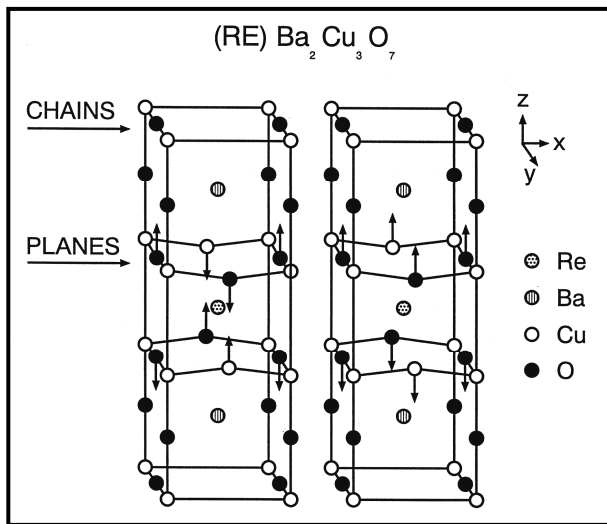
**Keywords:** critical current density, cuprate phase, stability, evaporation techniques, oxide substrates, physical vapor deposition

### 1. Introduction

It was the late morning of January 27<sup>th</sup> 1986 when G. Bednorz and K. A. Müller from the Zürich IBM Research Laboratories observed a drastic decrease of electrical resistance in a bulk ceramic La-Ba-Cu-O sample at about 35K. Complementary magnetic measurements showed a diamagnetic signal at 35 K, confirming Bednorz' and Müller's expectation of occurrence superconductivity in their sample. Their search for superconductivity in mixed valence complex oxides guided by concepts of the polarizability of oxygen in a perovskite-type structure in combination with correlations due to Jahn-Teller polarons came to a first successful breakthrough. The birth of this new class of superconductors was announced soon after in a publication with the cautious title "Possible high  $T_c$  superconductivity in the Ba-La-Cu-O system" in *Zeitschrift für Physik* [1]. This journal, albeit well known and respected in Europe, had not the high reputation compared to the high impact science journals such as *Physical Review Letters*, *Science* or *Nature*. The time elapsed between submission and publication, however, was less than 8 weeks and the revolutionary discovery received immediately a worldwide attention and appreciation culminating in the Nobel prize for Bednorz and Müller 1987. The discovery of superconductivity in the La-Ba-Cu-O system above 30K and the careful handling of the results shed some light on the superior abilities of Bednorz and Müller, both, scientifically as well as diplomatically. Soon after the confirmation of Bednorz and Müller's results by other teams, drastic pressure related effects on the electronic

properties of these compounds have been found yielding to an enhancement of the critical temperature,  $T_c$  [2]. This was the guideline for P. Chu to replace external pressure by chemical internal pressure. He and his co-workers synthesized the compound  $\text{YBa}_2\text{Cu}_3\text{O}_7$  [YBCO], a material with an even higher  $T_c$  of 92K [3]. The discovery of superconductivity in complex oxides at temperatures much higher than any metal, alloy or compound known so far opened a new era in condensed matter physics and chemistry with a tremendous application potential. It breaks the predicted barrier of  $T_c^{\text{max}} \sim 30\text{K}$  based on the BCS- theory with the electron-phonon coupling mechanism for Cooper pair formation at its core. At that time the record  $T_c$  was 23K for thermodynamically metastable  $\text{Nb}_3\text{Ge}$  and superconductivity in  $\text{MgB}_2$  at 39K was not yet found. This simple compound had been studied in the 1950s and had been on the shelves in some laboratories for various mundane purposes for decades, with no one suspecting its enormously valuable hidden talent until Akimitsu discovered its superconductivity [4].

The tremendous application potential of the cuprate superconductors can only be exploited if all technological problems ranging from thin film preparation to band and wire production can be mastered. Especially, a reliable thin film fabrication technology is regarded as a prerequisite for the large scale implementation of cuprate HTS materials into active and passive devices. The successful mastering of cuprate superconductor thin film technology opened the path for activities to explore the physics of other complex oxides materials such as the ferromagnetic rare



**Figure 1.** Crystal structure of YBCO. The arrows show the two different out of plane vibrational modes of the planar oxygen, giving rise to  $B_{1g}$  and  $B_{2g}$  phononic Raman modes.

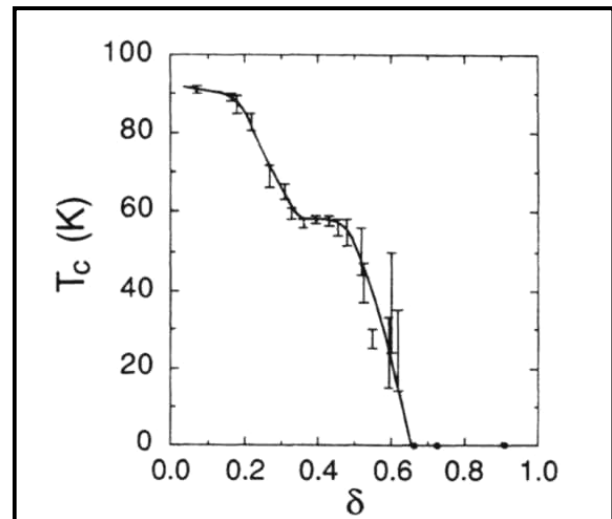
earth manganites, ferroelectrics and other oxides with strong electron correlation phenomena.

This paper concentrates on the problems and their solutions associated with HTS thin film preparation using physical vapour deposition [PVD] based techniques. MOCVD techniques as well as thick film preparation by liquid phase epitaxy have been treated separately by Hitchman [5] and Scheel [6]. From the materials side the paper is restricted to YBCO as prototype material representing the whole class. To prepare thin films of the other members of the family of cuprate superconductors, the Bi-, Tl- and Hg cuprates e.g., the same principles have to be obeyed with some modifications of the processes due the stability and volatility of the oxides of Bi, Tl and Hg, respectively [7].

In the literature there are several review papers published covering the early stages of the cuprate superconductor thin film deposition technology and some comparative evaluations of the different techniques [7-10]. Coverage of the more recent developments, however, is still missing. The paper is organized as follows. In a subsequent section the basic elements of the materials chemistry of the cuprate superconductors is treated, restricted to those relevant for thin film deposition. Section III covers the development of HTS thin film deposition technology, Sect IV deals with developments for practical tape applications and in Sect V some of the recent achievements in in-situ growth control and novel concepts for interface tailoring of oxides with different functionalities are discussed.

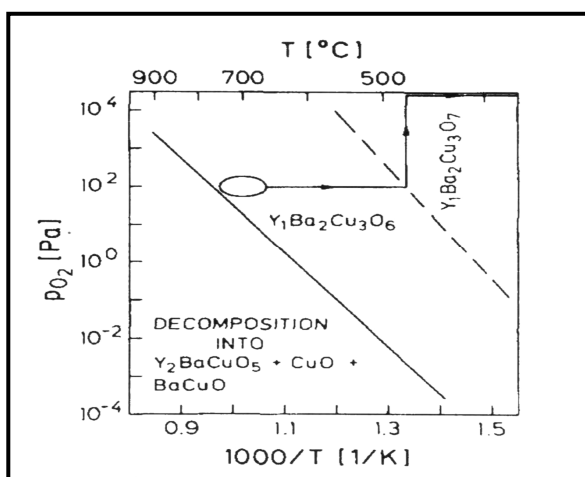
## 2. Crystal chemistry and phase stability of HTS compounds

All cuprate superconductors have in common a complex crystal structure derived from perovskite-type building blocks, the existence of  $\text{CuO}_2$  planes forming an



**Figure 2.**  $T_c$  for oxygen deficient  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  samples produced by quenching into liquid nitrogen from  $T = 530^\circ\text{C}$  into liquid nitrogen. (After Jorgensen et al. [12]).

antiferromagnetic ground state for the spins of the  $\text{Cu}$ -ions and the possibility to dope the  $\text{CuO}_2$  planes with electrons or holes supplied by the charge reservoir adjacent to them. Figure 1 shows the prototype structure of YBCO with the slightly buckled  $\text{CuO}_2$  planes separated by Y and the charge reservoir built by the  $\text{BaCuO}$  blocks with the  $\text{CuO}$  chains in the  $y$ -direction. There are plenty of detailed studies of the phase diagram of YBCO and the stabilization of the different phases, crystal growth and defects. An overview is given in [11]. Basically, the preparation of bulk ceramics of YBCO involves mixing of the adequate amounts of  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$  and  $\text{Cu}_2\text{O}$  with subsequent thermal sintering at  $\sim 900^\circ\text{C}$  followed by pressing the powder into the appropriate form and subject it to a further sintering in flowing oxygen. There are plenty of variations of this concept using different starting compounds (e.g. replacing  $\text{BaCO}_3$  by  $\text{BaF}_2$ ) and different heat treatment schemes for the solid state reaction. A critical step is the appropriate sintering time and temperature to ensure full oxygenation. This is critical since the doping of the  $\text{CuO}_2$  planes with holes depends on the filling of the chains with oxygen as charge reservoir. Figure 2 e.g. shows the dependence of  $T_c$  on the deviation  $\delta$  from the ideal stoichiometry  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  indicating a transition to a non-superconducting cuprate at  $\delta = 0.64$ . This transition is accompanied with a structural phase transition for the orthorhombic to tetragonal phase ( $0 < \delta < 0.64$ ). The plateau at  $T_c = 60\text{K}$  resembles a general feature in the  $T_c$  vs. hole doping curves with an anomaly at a doping level of  $1/8$  holes per  $\text{Cu}$  ion. From the practical point of view an easy, fast and non-destructive determination of  $\delta$  is of vital importance. This can either be accomplished by chemical means (mostly destructive such as titration or atomic emission spectroscopy) or making use of the oxygen dependence of the lattice parameters in YBCO [12]. An elegant alternative is



**Figure 3.** Oxygen partial pressure vs. temperature plot showing the CuO – Cu<sub>2</sub>O stability line and the area of single phase YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> deposition.

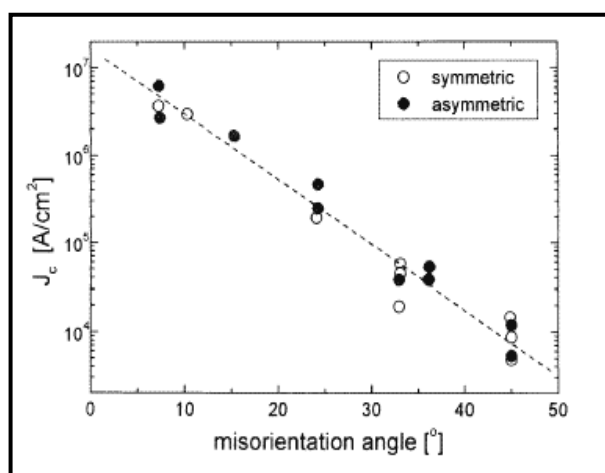
given by Raman spectroscopy where in one experiment not only the phase purity but also the oxygen concentration (shift of the Raman line associated with the apex oxygen) as well as the crystallite orientation easily can be determined [13]. The main requirements for the successful preparation of superconducting YBCO with a  $T_c$  of 90K consist in the accomplishment of three elements: (i) correct cation stoichiometry, (ii) correct crystal structure and (iii) correct oxygenation.

### 3. Basic requirements and HTS thin film preparation technology

#### 3.1 Basic requirements

The preparation of bulk material by mixing the elements or easily decomposing compounds and firing them at elevated temperatures is well understood [14], the deposition of films, however, with desired properties, including chemical and structural purity as well as high critical currents and atomically flat surfaces turned out to be much more complicated. Especially the spatial homogeneity and flat surfaces are prerequisites for large scale electronic applications are difficult to achieve.

The degree of sophistication in the deposition of high-quality thin HTS films is strongly determined by the fundamental physical properties of the material. First, the quasi two-dimensional (2D) nature of all oxide superconductors related to their layered structure leads to a large anisotropy in nearly all physical relevant parameters. The anisotropy ratios,  $\Gamma = \xi_{ab}/\xi_c$ , in the coherence length,  $\xi$ , as well as the penetration depth,  $\lambda$ , ranging from  $\sim 6$  for YBCO to over 100 for the Bi-, Hg-, and Tl –compounds, reflect the anisotropy of the Fermi surface, especially determined by the role of the CuO<sub>2</sub>-planes with their possibility to dope them either by holes or by electrons. The extremely short coherence lengths in all HTS cuprates of  $\xi_{ab}(0) = 2\text{nm}$  and  $\xi_c(0) = 0.3\text{ nm}$  for YBCO as well as  $\xi_{ab}(0) = 2-2.5$  and  $\xi_c(0) = 0.02-0.04$  for the three layer compound Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>10</sub> determine the length scale at which local variations in chemical



**Figure 4.** Critical current density in YBCO bicrystals as a function of misorientation angle at 77 K (after Dimos et al. [16]).

and/or structural properties will automatically result in a spatial variation of the superconducting properties. Metallic superconductors have values for  $\xi > 10\text{nm}$  and even the compound MgB<sub>2</sub> has  $\xi(0) = 5\text{ nm}$  and consequently it is much easier to build devices such as Josephson junctions with them. Because of the extremely small coherence length along the crystallographic c-axis, the current directions along the a–b direction (within the CuO planes) are utilized for most applications. This implies an epitaxial c-axis orientation of the films for nearly all applications.

Additionally, the superconducting properties strongly depend on variations in stoichiometry, especially in the oxygen concentration at a length scale determined by  $\xi$ . Further complications arise from the phase stability diagram of the cuprate superconductors [15]. Since all PVD-based deposition methods are vacuum techniques, certain requirements for temperature and oxygen partial pressure have to be fulfilled. Figure 3 shows the stability lines for the stability regions for the tetragonal YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> phase as well as the orthorhombic YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> –phase. A typical region for PLD deposition and cooling is indicated by the line in the temperature/oxygen diagram.

Finally, the usual growth mode of HTS films (Stranski-Krastanov) implies the coalescence of individual islands that can give rise to grain boundaries and/or even a granular structure of the film. Due to the stability requirements for the formation of Cu<sup>++</sup> during deposition and to avoid Cu<sup>+</sup> and the stable green phase Y<sub>2</sub>BaCuO<sub>5</sub> the film originally grows in the tetragonal phase YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> and during oxygen uptake (c.f. the line in figure 3) a tetragonal/ orthorhombic phase transition takes place resulting in a-b twinning. In the case of polycrystalline or textured HTS films, the intergranular properties clearly dominate superconducting properties such as the transport current density  $J_c$  or microwave surface resistance  $R_s$ . However, even for epitaxial films small-angle grain boundaries cannot be avoided. Even small angle grain boundaries have an effect on  $J_c$  as shown in figure 4. With

**Table 1.** Properties of substrate materials suitable for cuprate superconductor thin film deposition.

<i>Substrate materials</i>	<i>Thermal expansion coefficient</i> ( $10^{-6} \text{ C}^{-1}$ )	<i>Melting temperature</i> ( $^{\circ}\text{C}$ )	<i>Available substrate size</i> (mm diameter)	<i>Misfit to YBCO</i> (%)	<i>Twinning</i>	<i>Chemical stability</i>
SrTiO <sub>3</sub>	9.4	2080	50	1.4	no	good
YSZ	11.4	2550	100	6	no	good
MgO	14	2825	>30	9	no	poor
$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	9.4	2050	100	6-11		good
LaAlO <sub>3</sub>	10-13	2100	100	2	yes	good
LaSrGaO <sub>4</sub>	10	1520	15	0.26	no	good
LaSrAlO <sub>4</sub>	7.55	1650	10	2.7	no	good
LaGaO <sub>3</sub>	9	1715	40	2	yes	good
NdGaO <sub>3</sub>	9-11	1670	50	0.04	no	good
PrGaO <sub>3</sub>	7-8	1680	10	0.3	yes	good

increasing misorientation angle  $J_c$  decreases [16] by orders of magnitude. The consequences for HTS base wire and tape fabrication are obvious.

Currently, much effort is undertaken to fabricate tapes on textured substrates facilitating a controlled grain growth to avoid  $J_c$  reduction.

These extraordinary properties require special precautions for the deposition process. They certainly depend on the application for which the film will be used. For most applications epitaxial films are needed without large-angle grain boundary, secondary phases and outgrowths, high critical current density  $J_c$  or low microwave surface resistance  $R_s$ . In a number of cases, smooth surfaces are needed (e.g. for submicrometer patterning and multilayers) or defects have to be implemented in order to provide pinning centers or to release internal stress in the sample, which might lead to micro cracks if a critical thickness is exceeded.

### 3. 2 Substrate requirements

For the development of a reliable deposition technology for high-quality HTS thin films, the choice of the substrate material is of primary importance. The basic requirements for the substrates can be summarized as follows:

- crystallographic lattice match between HTS film and substrate to avoid strain-induced defect generation,
- similar thermal expansion coefficients of film and substrate,
- no chemical interaction at the interface between film and substrate,
- suitably polished surfaces, structurally as well as chemically stable.

Depending on the application of the films, specific requirements for the substrate must be fulfilled. For some passive electronic applications twinning of the

substrates should be avoided, the available size of the substrate determines the cost per device, or its cost itself is of importance. For microwave applications the dielectric properties, surface quality and available size of the substrate are relevant. Generally we can distinguish between two classes of substrates: (i) those compatible with the cuprate thin film deposition technique without additional buffer layers and (ii) those where a buffer layer is required to accommodate large lattice mismatch or to prevent chemical interaction between substrate and HTS material. Deposition onto compatible substrates is generally easier. Typical candidates are LaAlO<sub>3</sub>, SrTiO<sub>3</sub> and MgO for YBCO deposition. In table 1 some of the most frequently used substrates and their properties are listed.

The deposition of cuprate superconductors onto a number of technically interesting substrate materials (e.g. metal tapes, Si, GaAs, Al<sub>2</sub>O<sub>3</sub>) requires a previous coating with an adequate buffer layer which facilitates epitaxial growth (e.g. by reducing the lattice mismatch between substrate and HTS material) and provides a sufficient barrier against interdiffusion of substrate and HTS material. Two different approaches are considered for the choice of buffer layers. First, a material is chosen which is similar to YBCO with respect to chemical and structural properties. One of the few promising candidates for such a buffer is the semiconducting perovskite PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> (PBCO). PBCO layers are also good candidates for YBCO multilayer fabrication [17, 18]. Its resistivity can be improved by partial substitution of Pr by Y without loss of chemical and structural compatibility. Exploiting the partial substitution of Y by Pr in the YBCO system offers a wide field of tailoring the electronic properties of the buffer and influences the superconductivity at the interface of both layers. In the case of sapphire substrates, however, YBCO films on

PBCO/sapphire exhibit higher  $R_s$  and lower  $J_c$  values than observed for YBCO films of reasonable quality irrespective of the fact that the Al diffusion into the YBCO film is blocked by PBCO buffer layers on sapphire. The alternative approach uses oxides with a cubic structure and lattice parameters comparable with either the cubic axis or the diagonal of the (001) orthorhombic plane of YBCO are chosen. Among a large number of candidates MgO, YSZ ( $ZrO_2$  stabilized with ~9 mol% of  $Y_2O_3$ ) and  $CeO_2$  are the most attractive ones. Whereas the lattice parameter of MgO is closer to that of sapphire, those of YSZ and  $CeO_2$  match that of YBCO.  $CeO_2$  has proven to be one of the most effective buffers owing to its favorable thin-film growth characteristics, minimal chemical interaction and good lattice match with most HTS materials.

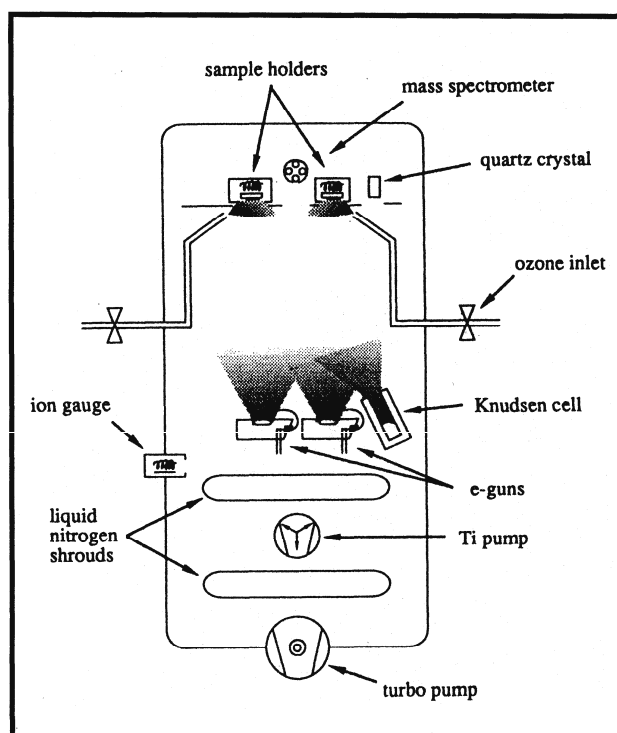
### 3.3 Deposition techniques

Nearly all commonly used thin film deposition techniques have been more or less successfully employed for cuprate superconductor thin film and multilayer fabrication, e.g. thermal and e-beam evaporation or co-evaporation, thermal or laser molecular beam epitaxy (MBE), on-axis and off-axis high-pressure sputtering, on-axis and off-axis pulsed laser ablation. The typical preparation regime in the  $p_{O_2}/T$  diagram is grouped around the ellipsoid in figure 3 for the *in-situ* routes. While the *in situ* deposition route is used for the majority of YBCO and BiSrCaCuO film preparations, the *ex situ* route is very widely used for TlBaCaCuO [19] and HgBaCaCuO [20] films and only occasionally for YBCO deposition. Essentially the *ex situ* route uses the same deposition steps as the *in-situ* method, the deposition temperature, however, is drastically reduced to around 300°C to 400°C resulting in microcrystalline or amorphous precursors that are subjected to an *ex-situ* annealing step at appropriate temperatures. For instance, the preparation of TlBaCaCuO (e.g.  $Tl_2Ba_2CaCu_2O_8$ ) films can be achieved by deposition of an amorphous precursor film onto a room temperature or slightly heated substrate followed by annealing in oxygen and  $Tl_2O$  vapor [21].

*In-situ* deposition techniques usually also apply two steps, i.e. the deposition at high temperature (substrate temperature during deposition of YBCO range depending on the process pressure from 700°C to 780°C followed by a post-deposition oxygen treatment during which the phase transition from the tetragonal to orthorhombic state takes place.

### 3.4 Reactive evaporation

The simplest approach is to use resistively heated boats as thermal sources or electron beam guns for the metallic constituents combined with a rate control using quartz-crystal microbalances and computer-controlled tuning of the heating current. A typical set-up is given in figure 5 equipped with  $e^-$  guns and a thermal evaporator. This system is designed for single layer deposition, the implementation of additional  $e^-$  guns opens the way for



**Figure 5.** Thermal evaporation system for cuprate superconductor thin film preparation.

heterostructure and superlattice fabrication. Reactive evaporation is an excellent technique especially to finely tune the composition of the individual layers and to grow large area films. One fundamental problem is the appropriate amount of reactive oxygen in conjunction with the requirement of the operation conditions for the  $e^-$  guns and the long mean free path of the evaporant. A very effective implementation of the evaporation technique has been realized by Kinder et al. [22] utilizing a black-body-type rotating disk heater which has a deposition section and a oxidation pocket with a narrow opening so that in the oxidation section a relatively high oxygen pressure of 1Pa can be maintained whereas in the chamber the background pressure is lower by a factor of 100. Evaporation techniques require an accurate method of controlling the relative deposition rates of the constituents involved. This can be done by quartz crystal monitors, quadrupole mass-spectrometers or optical absorption measurements.

### 3.5 Molecular beam epitaxy/ atomic layer epitaxy [MBE / ALE]

Due to the short coherence length in all HTS superconductors especially for Josephson junction applications and all heterostructure and superlattice work one needs to deposit ultra thin layers with interfaces as perfect as possible. Backed by the experiences in semiconductor superlattice and heterostructure fabrication reactive MBE has been demonstrated to be one of the most successful techniques to accomplish this goal. [23, 24]. Reactive MBE is similar to reactive

evaporation with the exception that the pressure during evaporation is low enough to ensure a mean free path of the species emitted from the sources longer than the source - substrate distance. Furthermore, the walls of the deposition chamber have to be cold enough that no reemission of adsorbed species can take place. Typical working pressures for reactive MBE are below  $10^{-3}$  Pa. A practical MBE system for HTS SL fabrication is shown in figure 6. To provide molecular beams of the elemental constituents radiatively heated effusion cells are used and the molecular beams are chopped by computer controlled mechanical shutters. The advantage of effusion cells over resistively heated boats is the more homogeneous momentum distribution of the evaporant impinging the substrate and the easier evaporant flux control. For successful atomic layer epitaxy it is necessary not only to monitor the relative ratios of the molecular beams of the different constituents but also the relative fluxes of the beams. Spectroscopic techniques such as measurement of absorption or emission of visible or UV characteristic radiation is applied in addition to conventional quartz-crystal monitors. Modern MBE systems for HTC SC research combine flux-controlled deposition from up to ten effusion cells with sophisticated in-situ analytical tools such as LEEM/PEEM/LEED and TOF-ISARS. One of the most advanced systems of this type is the combinatorial MBE [COMBE] of Oxxel [25]. The reactive MBE technique represents the most elegant and clean for HTS SL fabrication and due to the low kinetic energy of the particles impinging the substrate [ $\sim 0.1$  eV], consequently a high quality of the interfaces can be expected. The MBE approach requires a special source for reactive oxygen, mostly ozone generators are used and an ozone flux is directed towards the substrate. MBE systems for HTS SL fabrication require a major capital investment.

### 3. 6 Sputtering

Sputtering-often described as playing billiard with atoms-is the ejection of target atoms by the impingement of ions from a persistent glow discharge with kinetic energies larger than the binding energy of the target atoms. It is a conventional widely used method where the film composition is normally expected to be equal to the target composition at least for multicomponent metallic targets. As sputtering gas usually Ar is used, desired chemical reactions of the sputtered atoms/ions in the plasma can be achieved by adding reactive gases to the sputtering gas. In the case of YBCO and other multicomponent oxide systems tremendous problems arise from the formation of negatively charged particles at the target [cathode] side. Elements with a large electronegativity difference such as oxygen and the alkaline earth metals form negative ions which are accelerated away from the target by the potential difference of the cathode dark space. This energetic particle flux is directed to the substrate in conventional sputtering geometries leading to selective resputtering of the growing film which modifies the film composition or

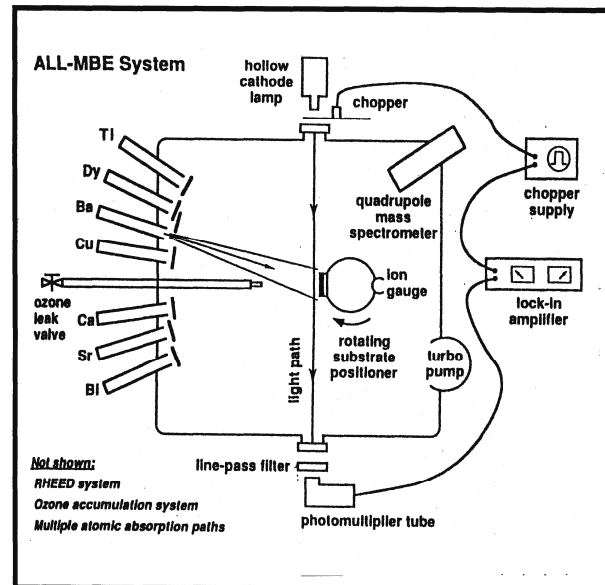


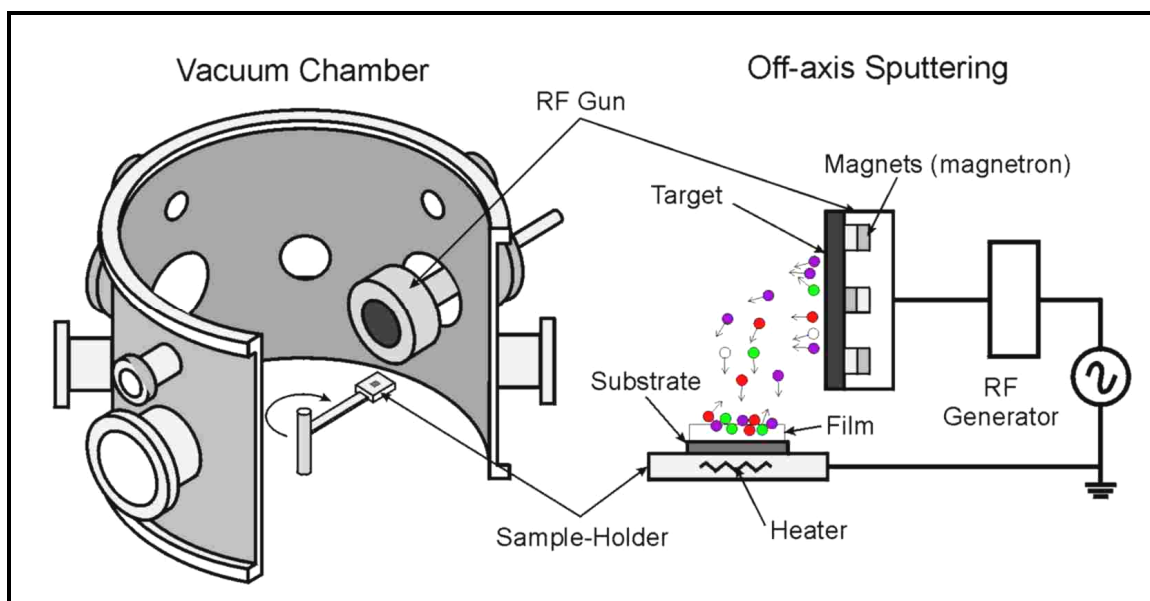
Figure 6. Schematic molecular beam epitaxy system for layer-by-layer deposition (after Bozovic [23]).

gives rise - in extreme cases - to etching of the substrate rather than deposition. To overcome these problems at least four different routes are used: (i) to work at gas pressures high enough to reduce the kinetic energy of the ions striking the substrate below the binding energy [24], (ii) to place the substrate off-axis so it will not face the cathode [A very convincing realization of this idea is the inverted hollow cathode arrangement by Geerk 25], (iii) to design the system for a minimum discharge voltage [26] and (iiii) to adjust the target composition for a compensation of the resputtering effects [27]. Practically, a huge variety of different arrangements of target substrate position and target configurations have been applied or tried for in situ processes. The sputtering source configurations include multitarget arrangements using metal, metal alloy or metal oxide targets, single ceramic 1-2-3 targets, single off stoichiometric YBCO targets and stoichiometric 1-2-3- YBCO hollow cylindrical targets. A comprehensive review covering the developments til around 1988 is given by Leskelä [7]. In figure7 a typical off-axis sputtering system is sketched.

A new type of configuration designed for an in situ process has been introduced by Wagner et al. [30]. Here, 3 magnetron RF sources with stoichiometric YBCO 1-2-3 ceramic targets are used in conjunction with the substrate placed somehow off-axis. This arrangement is used for homogeneous large area deposition [approximately 2 inch substrates]. In figure 8 the view of the appropriate cluster flange for the sputtering gun arrangements is given.

### 3. 7 Pulsed laser deposition [PLD]

In pulsed laser deposition techniques short pulses-typically 10-30 ns of UV light are focused onto a target of desired composition. The light is absorbed according to its penetration depth and a thin layer of



**Figure 7.** (color online) Scheme of an off-axis sputtering system.



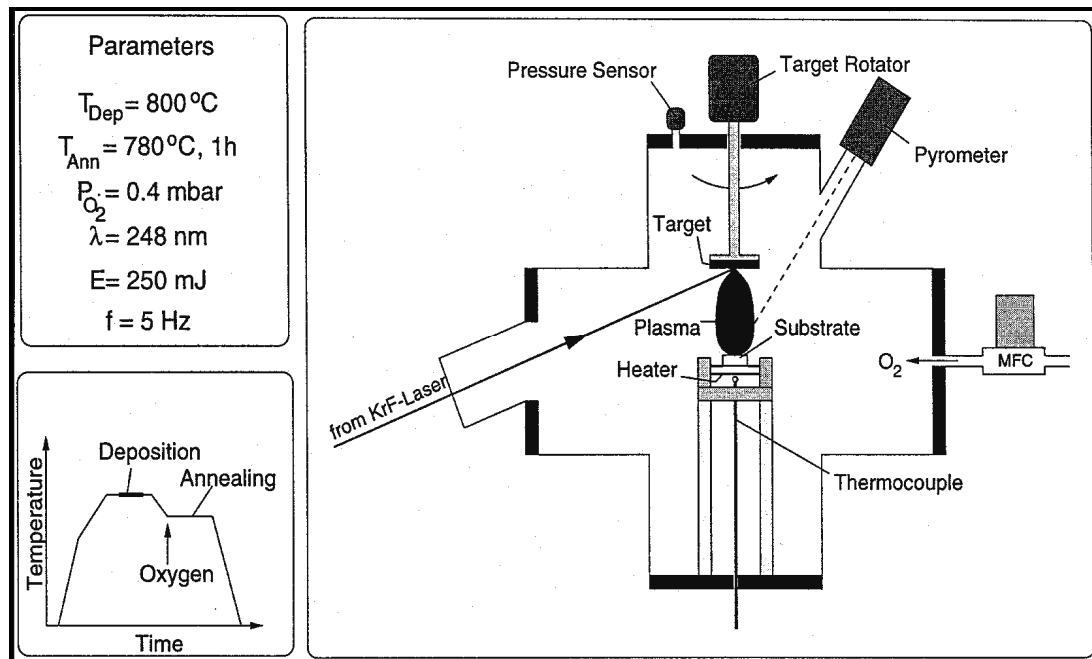
**Figure 8.** (color online) Cluster flange arrangement for 3 sputtering guns.

super-heated material is formed which expands into the chamber in the form of a forward directed luminous laser plume. This technique, originally introduced by Dijkamp et al. [31] for the deposition of YBCO single layers has experienced a wide spread use for all kinds of oxide thin film deposition. A general description of the application potential of PLD and the processes taking place during the ablation process are found in the book of Bäuerle and references herein [32]. Using typical deposition conditions [ $T_D = 760^\circ\text{C}$ ,  $p_{O_2} = 20\text{Pa}$ ] growth rates of  $\sim 0.25\text{nm/sec}$  are achieved using a 5 Hz pulse repetition rate. Due to the stoichiometric ablation from the target it is quite simple to achieve chemical composition identity of target and film – provided no volatile species are formed. Heterostructures and superlattices can easily be prepared using this method. Computer-controlled target exchange systems are used and in conjunction with a separately growth rate determination by counting pulses. This is possible because the nominal

thickness of the ablated material per pulse is much smaller as compared to the individual building blocks of the HTS materials, simple pulse counting is sufficient for the thickness monitoring. This procedure however requires constant laser fluency per pulse which is dependent on the quality of the laser used. Systematic improvements of growth control can be achieved by the implementation of a Reflection High-Energy Electron Diffraction (RHEED) system.

The advantage of the PLD approach is its simplicity, flexibility and the possibility to switch from one material to the other just by replacing targets of typical sizes  $\sim 15\text{mm}$  diameter and 5 mm thick. They can be fabricated in house usually, so new material combinations can be assessed quite quickly. The disadvantage of the PLD technique is seen in the restriction to small substrate areas of  $\sim 2\text{cm}^2$  and in the homogeneity of thickness and composition. Additionally, the high kinetic energies of the particles impinging the substrate [10-60 eV] can cause re-sputtering effects if the incident laser beam fluency is too high. As a fundamental problem the formation of droplets of the deposited material has to be considered. The droplet formation is a complex matter (partially covered in the book of Bäuerle) [32] and several techniques have been employed to overcome this problem. The most successful ones are either the particle energy filtering [33] or optimizing the laser-beam homogeneity and shape control by external beam homogenizers. The PLD approach is seen as an ideal low cost tool for exploratory research and development. In figure 9 a standard PLD system designed for single layer oxide thin film deposition is shown which easily can be upgraded for heterostructure and superlattice thin film work by implementing a computer controlled target rotation and target exchange system. Furthermore, the system is equipped with a far infrared pyrometer to





**Figure 9.** Schematic drawing of a PLD system for complex oxide thin film deposition. Note the pyrometer facing the sample stage.

measure the actual substrate (film) surface temperature. A computer controlled feedback loop to the power supply ensures a constant de-position temperature at the growth front. The adjustment for the different emission coefficients of substrate and film is a part of the program. Efforts to extend PLD to large area substrates have been made by translation and rotation of both, targets and substrate. So far, however, scaling-up the substrate sizes has been achieved more successfully by sputtering and evaporation techniques rather than by PLD.

### 3. 8 Comparison of the in-situ techniques

Each technique has its own advantages and disadvantages and its own potential. PLD is the most flexible and has the potential to produce films very rapidly with consistently high quality in  $T_c$ ,  $R_s$  and  $J_c$ . Because of the explosive nature due to the impact of the laser pulse on the material there are still some difficulties to overcome the droplet problem. For the majority of present research applications it has to be proven to be a very suitable technique. Sputtering on the other hand, can produce films of slightly higher structural quality and does not suffer the droplet problem of laser ablation, but it suffers from the inherently low (typically  $20\text{--}300\text{ nm h}^{-1}$ ) deposition rate due to the indirect geometries or high levels of thermalization required. Nevertheless, it is being widely used for the deposition of compounds (e.g. nitrides and oxides) comparable with HTS material as the workhorse technique because it is reliable, cheap and relatively easy to run automatically and can be scaled up to areas with one dimension up to the m range. Evaporation and MBE techniques are quite difficult

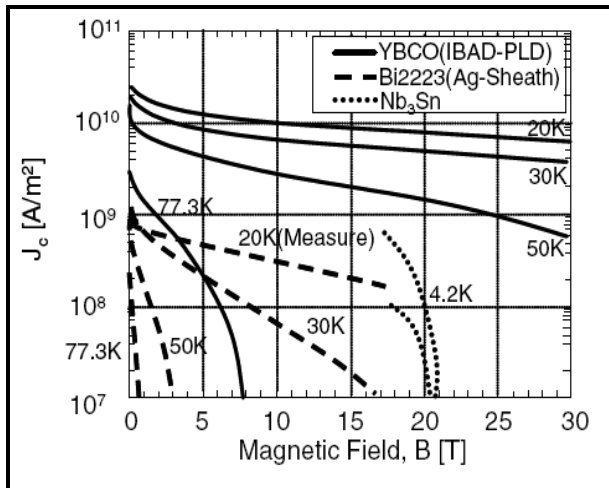
undertakings but are very scientifically rewarding because one may easily incorporate *in situ* analysis, particularly RHEED which can give a continuous signature of the perfection of the structure being grown. Also, direct control of the composition can be incorporated. The main difference of the techniques, however, -aside of being either continuous or pulsed, which affects the growth in some ways- lies in the kinetic energy of the particles ( atoms, ions ) impinging the substrate and the growing film. This in turn has consequences for the supersaturation of the particle beam which in turn influences the growth itself.

### 4. HTS thin film preparation for technological application

Since the discovery of oxide superconductors in 1986, research in material science fields has proceeded and developments for applications have been carried out extensively. One of them is the evolution into praxis of coated conductors and tapes for power transmission as well as solenoid coil fabrication. The second generation development of coated conductors uses the  $\text{REBa}_2\text{Cu}_3\text{O}_{7-\delta}$  system which is expected to overcome the weak points using Bi-cuprates. The Bi-cuprates mainly suffer from low critical current densities under high magnetic fields in the range of liquid nitrogen temperatures. Figure 10 shows typical  $J_c$ -B characteristics of tapes of the Y and the Bi systems.

The  $J_c$  values of Bi-2223 wire decrease by two orders of magnitude in external magnetic field of 1 T in the high temperature region of 77 K. On the other hand, the degradation of  $J_c$  values of the Y system has been suppressed within one order even at 3 T. However, even



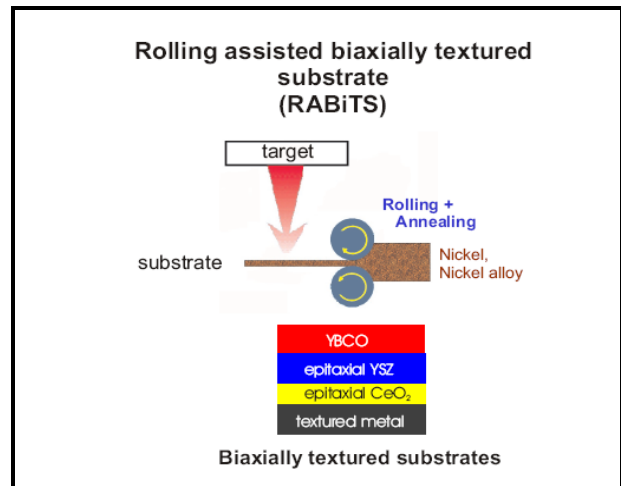


**Figure 10.** Magnetic field dependence of the  $J_c$  value at various temperatures (taken from [34]).

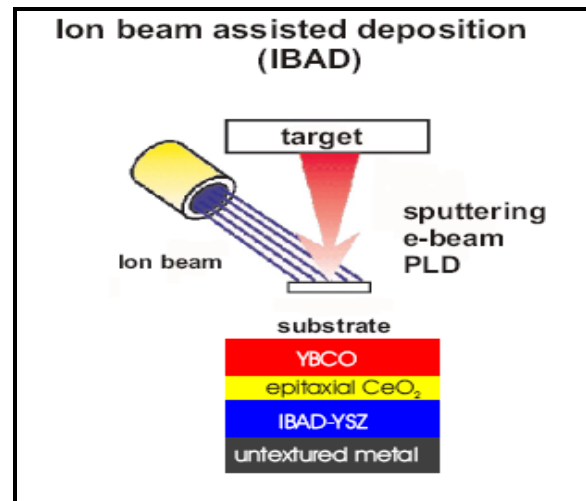
in the Y system, degradation of the  $J_c$  values depends strongly on the crystal grain misalignment. One of the significant features of the RE123 in the development of coated conductors is the large anisotropy of electromagnetic properties. Therefore, the in-plane crystal grain alignment is required in order to attain full material characteristics of RE123. This requirement has to be satisfied in long tapes for applications of coated conductors. In order to control a crystal grain alignment of the superconducting layer, two distinct technologies exist including fabrication of textured metallic substrates such as RABiTS™ (rolling-assisted biaxially textured substrates) [35,36] and crystal grain alignment of a buffer layer on a non-textured high strength metallic substrate by IBAD (ion beam assisted deposition) [37,38] and/or ISD (inclined substrate deposition) [39,40]. Figure 11 represents the scheme for the RABiTS approach. These coated conductors have a multilayered film structure, that is an RE123 superconducting layer fabricated on a metal substrate with some buffer layers. The metal substrate gives a mechanical strength and crystal grain alignment in some cases, and the roles of the buffer layers are the crystal grain alignment and prevention of chemical reaction as well as crack generation.

Alternatively, the IBAD method is a process for deposition of an in-plane aligned buffer layer by applying an additional assisting ion beam from an appropriate direction during the deposition of the buffer layer. This IBAD process for depositing the in-plane aligned YSZ buffer layer was originally established by the research team of Fujikura in 1991. The IBAD-YSZ process gives an excellent crystal grain alignment with a small grain size, which is suitable for maintaining high performance in a long tape. Figure 12 shows a sketch of the principle of IBAD.

However, the slow deposition rate is still a problem from an engineering point of view. The research activities currently concentrate on the exploration of



**Figure 11.** (color online) Schematic sketch of the RABiTS approach for coated conductors.

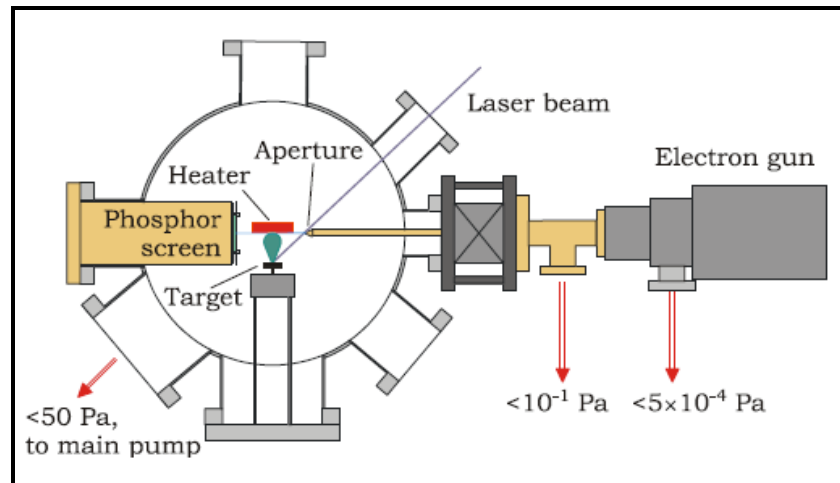


**Figure 12.** (color online) Sketch of the principle of IBAD.

achieving higher gross production rates by increasing the area of deposition. Recently, a high production rate of  $1 \text{ m h}^{-1}$  was achieved by the development of large-scale IBAD equipment and the discovery of a more appropriate buffer layer material,  $\text{Zr}_2\text{Gd}_2\text{O}_7$ . Moreover, this new material can give a better crystal grain alignment even in a thinner film. This leads to a higher production rate.

## 5. In - situ cuprate thin film growth control and recent developments

During the past 5 years an increasing demand for improved growth control emerged. This was mainly triggered by the attempts not only to deposit single layer cuprate thin films but also to technologically enable the concept of molecular engineering of oxides. Especially for the cuprate superconductors with their intrinsic layered structure consisting of the  $\text{CuO}_2$  planes and the charge reservoir this has a special importance. The first

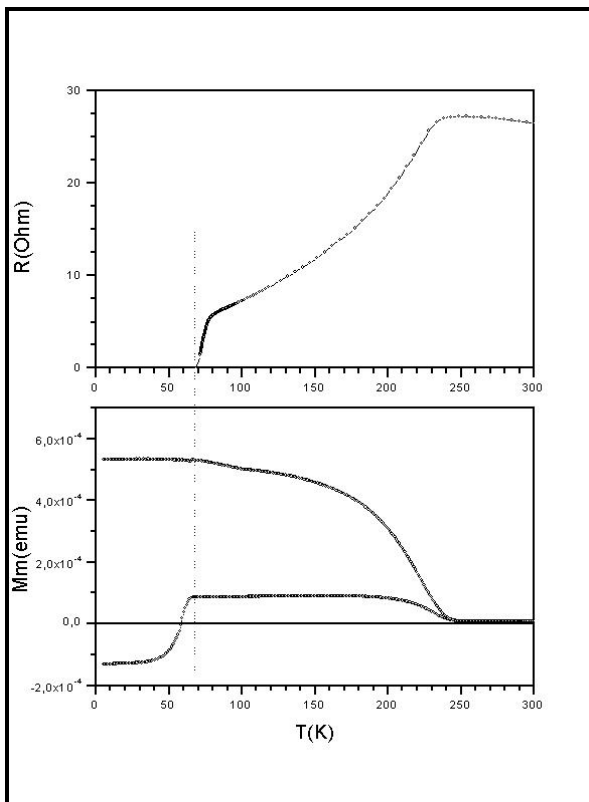


**Figure 13.** (color online) Sketch of the configuration for PLD-RHEED (taken from TSST homepage).

activities have been grouped around the concept of block-by-block deposition i.e. to grow the known materials using a sequential deposition technique so that the atomic monolayers are stacked artificially on top of one another in a sequence defined by the structure of the unit cell [41]. Additionally this concept was used to search for new stacking sequences and thus for new materials with potentially higher  $T_c$ . From the technological point of view an in-situ growth control is mandatory for this purpose and comparing oxide growth techniques with semiconductor heterostructure and superlattice growth techniques it was clear that Reflection High-Energy Electron Diffraction (RHEED) control would be the method of choice. RHEED is a very widely used technique for the study of surfaces of materials. By virtue of the intensity variation of the diffraction spots, caused by roughness of the surface, RHEED can be used to study in-situ the growth mode of materials. Furthermore, by studying the diffraction pattern itself, surface reconstructions can be identified. Up to recently, however, it was not possible to use RHEED in combination with deposition techniques that require high background pressures, such as Pulsed Laser Deposition (PLD). The increased scattering of the electrons would fade out the diffraction pattern before it could be detected. In 1997, the Low Temperature Division at the University of Twente developed a system, which allows RHEED operation also in higher pressure environments [42]. The system consists of a differentially pumped RHEED gun combined with minimizing the distance between the sample and the RHEED screen. A sketch of a typical high pressure RHEED system is given in figure 13.

The application of RHEED techniques for oxide thin film growth control enables not only to grow single layer complex oxides with perfect layer termination and thus surface quality but also to carefully tailor interfaces between different oxide materials. That can give rise to novel physical phenomena and functionalities not exhibited by either of the constituent materials alone.

The combination of oxides with ferromagnetic and superconducting order may serve as an example. For a long time magnetic order and superconductivity (SC) have been regarded as antagonistic by nature. In conventional s-wave superconductors local magnetic moments break the spin singlet Cooper pairs and thus strongly suppress superconductivity. Therefore, uniform ferromagnetism (FM) and SC can not coexist. Similarly, injection of spinpolarized quasiparticles into s-wave SC's results in a suppression of superconductivity due to the breaking of time-reversal symmetry of the Cooper pairs. Recently, however, there was growing interest in exploring the physics of the (ferro) magnetic superconductor  $\text{RuSr}_2\text{GdCu}_2\text{O}_8$  with a charge reservoir block containing magnetically ordered  $\text{Ru}^{5+}$  spins intercalated by the  $\text{CuO}_2\text{-Gd-CuO}_2$  layers which are believed to cause SC [43, 44, 45]. They undergo a magnetic transition at 130-140K followed by a superconducting transition at 20K-50K. Low temperature magnetization studies show a significant ferromagnetic component [6] whereas in recent neutron diffraction experiment an antiferromagnetic structure associated with the Ru sublattice has been observed [46]. The interplay of magnetic and superconducting properties of these compounds is a topic of current concern. Due to the layered nature of the  $\text{RuSr}_2\text{GdCu}_2\text{O}_8$  compound the properties of this material can be mimicked by superlattices (SL) consisting of individual superconducting and ferromagnetic layers. Modifications of the modulation length of the SC and FM layers, respectively, are an experimental tool to tailor the coupling between the ferromagnetic and superconducting layers in a stack. Both have a highly anisotropic Fermi surface and the SC part is anisotropic d-wave. The advantages of the combination cuprate/manganite SL's is seen in their all oxide nature, crystal structure compatibility and partially adjustable lattice parameters of La-manganite part. The coexistence of both ordering phenomena is demonstrated in figure 14 for an  $\text{YBCO/LCMO} [10\text{nm}/10\text{nm}]_5$  superlattices [47].



**Figure 14.** Resistance vs. temperature and magnetization vs. T for a YBCO / LCMO superlattice.

The temperatures for both transitions,  $T_c$  as well as  $T_{Curie}$  are reduced as compared to single layer films resulting from an electronic interaction at the interface.

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