Materials Engineering Problems in Crystal Growth and Epitaxy of Cuprate Superconductors

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Introduction

The discovery of superconductivity in yttrium barium cuprate above the boiling point of liquid nitrogen by Wu et al.[1] initiated a race in the search for higher critical temperatures (T_c) which was singular in the history of science. Since the ceramic superconducting pellets could be prepared nearly overnight and superconductivity easily demonstrated with liquid nitrogen and a levitating magnet, a great deal of effort went into garnering funds for a "new technological era." High T_c superconductivity (HTSC) was expected to have applications in many areas of our life, be it for energy transport and high-power generators, transformers, current limiters, or for ultrafast computers and communication technology, or in medicine for NMR tomography and for SQUIDs in magnetic encephalography. Large-scale uses were also foreseen, such as levitation for trains, magnetohydrodynamic propulsion in ships, and applications for fusion reactors. Thousands of physicists and engineers searched for new materials with high T_c, and explored thin-film preparation by physical vapor deposition. In the early phase only a few scientists recognized that materials engineering problems would greatly hinder the development of applications of the cuprate superconductors. Most early efforts on HTSC went toward physical investigations of samples (crystals, layers, sheets, wires, etc.) which due to their complexity could not be reproducibly prepared, and which were not adequately characterized (see the section on Characterization). The Bi-, Tl-, and Hg-containing cuprates with T_c up to 135 K, for example, were found empirically, not by physical understanding of the HTSC phenomenon. Applications of HTSC have been limited to very specific areas, but a concerted effort should reveal opportunities for the materials research and superconductivity communities. Significant applications could be developed which in the long run would also benefit fundamental physical investigations of the HTSC phenomenon.

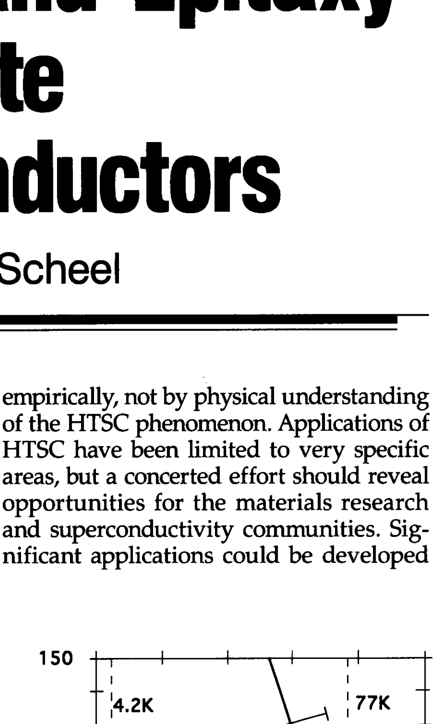

Figure 1. Temperature dependences of the upper critical fields of the classical superconductors NbTi and Nb_3Sn, for the Chevrel phase $PbMo_6S_8$, and for YBCO with the layer structure (after Reference 2).

This article discusses the causes of the materials engineering problems in HTSC development: complexity and limited stability ranges of HTSC compounds in combination with stringent requirements based on the very short coherence lengths of high T_c superconductors. The article then discusses specific materials engineering problems related to crystal growth and epitaxy, such as phase diagrams, crucible corrosion, growth stability, and strain problems in connection with epitaxy, oxidation, and phase transitions.

Complexity and Limited Stability of HTSC Cuprates

Superconductivity was first discovered in metals (Hg, Pb), then in binary compounds (NbC, NbN, A15 type compounds like Nb_3Sn) with critical temperatures up to 23 K in Nb_3Ge. Superconducting NbTi wires and coils are applied in medicine and in various technologies; the materials engineering problems could be solved for these relatively simple intermetallic compounds and alloys. The upper critical fields, which limit the current-carrying capability of NbTi and Nb_3Sn, are 12 T and 22 T at 4.2 K, respectively. With the discovery of the ternary Chevrel phases like $PbMo_6S_8$ with critical temperatures of about 15 K and critical fields above 50 T (see Figure 1), the development of very high magnetic field applications was envisaged. However, unsolved chemical stoichiometry and materials engineering problems have so far prevented large-scale applications despite serious efforts. The discovery of the cuprate superconductors brought a T_c above the boiling temperature of liquid nitrogen, and also the vision of ultrahigh magnetic fields (see Figure 1), even at liquid-nitrogen temperatures. However, wires with the corresponding crystallite orientation (Figure 1) and electron percolation could not yet be developed because of the difficulty of stoichiometry control and complexity of the composition with four, five, or even more constituents. Figure 2 shows the historical development of critical temperatures of superconductors which become increasingly complex with increasing T_c.

The relatively strong metal-oxygen bonds require processing the oxide compounds at high temperatures to mobilize the species for recrystallization, epitaxial growth, and bulk crystal growth. Figure 3 shows that with increasing T_c the thermodynamic stabilities of the superconductors, as indicated by the melting or decomposition temperatures, decrease. This can be attributed to the complexity of compounds (the highest

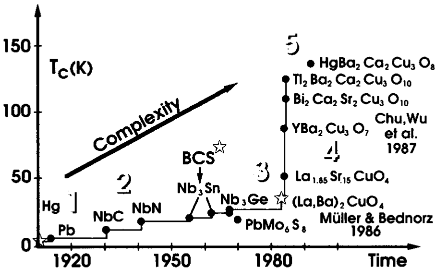

Figure 2. Historical development of superconductors, with Nobel prizes indicated by stars. Increasing T_c requires increased chemical complexity of constituent elements, shown as numbers 1–5. BCS stands for the Bardeen, Cooper, and Schrieffer theory[4] on classical superconductors.[3]

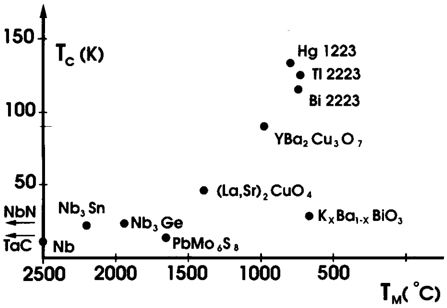

Figure 3. Relationship of the critical temperature T_c and the melting or decomposition temperatures T_M of superconductors.[3]

melting points are found in binary compounds like NbN and TaC), but it is probably also related to the mechanism of high-temperature superconductivity, which is observed only in relatively unstable compounds. The combined effect of complex composition, complex (layer) structure, and limited thermodynamical stability confronts materials scientists with great difficulties which are increasing with increased T_c. From Figure 3 and from the last years' experiences one could assume that technologically useful superconductivity may not pass the critical limit of about 150 K. Unfortunately, physics is far from understanding the phenomenon of high T_c superconductivity, i.e., superconductivity above the 35 to 40 K limit of classical superconductivity explained by the Bardeen-Cooper-Schrieffer theory.[4] Therefore, practical HTSC compounds could not be predicted, and the presently known high T_c superconductors have been found empirically, by simple crystal-chemical variational principles starting from the superconductivity accidentally discovered in a mixture of La-Ba-Cu-O phases and CuO in 1986.[5] This mixture fortunately contained a sufficient amount of the La-Ba-Cu-O phase with the right dopant concentration to give a temperature dependence of the resistivity, which could "possibly" be related to superconductivity.

The following emphasizes the HTSC compound $YBa_2Cu_3O_{7-x}$, known as "YBCO," because it is the most widely investigated compound and is regarded as a candidate for numerous applications. YBCO is a representative of the $RBa_2Cu_3O_7$ superconductors (R = rare earth), the so-called 123 compounds. Many of the problems with YBCO are similar to those of the other major classes of high T_c compounds with T_c above the boiling point of liquid nitrogen: Bi-Sr-Ca-Cu-O with T_c up to 115 K, Tl-Ba-Ca-Cu-O with T_c up to 125 K, and Hg-Ba-Ca-Cu-O with T_c up to 133 K, which will be treated very briefly at the end of this review.

The thermodynamic stability range of YBCO limits the parameters in synthesis and crystal growth. $YBa_2Cu_3O_{7-x}$ as synthesized at high temperatures has x values of 0.7 to 1, is tetragonal, and is not superconducting. By oxidation (which will be discussed later), x is reduced to 0.1 to 0, and by cooling through the phase transition range around 650°C, YBCO becomes orthorhombic. Only this oxidized phase is superconducting at about 92 K. I will not discuss the crystallographic aspects, site occupancies, and oxygen ordering effects, but limit my treatment only to those factors relevant to growth and to applications. The thermodynamic stability limits of the orthorhombic and tetragonal YBCO phases as a function of temperature and oxygen partial pressure are given in Figure 4. In this diagram (modified after Reference 3), the growth conditions for bulk crystals and liquid-phase epitaxy (LPE) as well as for epitaxial growth by chemical and physical vapor deposition methods are inserted. In vapor growth the growth temperatures can still be relatively high at sufficiently high oxygen partial pressures in metalorganic chemical vapor deposition (MOCVD). In the physical vapor deposition methods (PVD), with increasing vacuum and therefore lowered oxygen pressure, the surface mobilities of the oxide species are so low that the lateral distances between growth steps become very small, less than 30 nm. A few groups realized that in CVD or PVD of YBCO very near to the upper stability limit, larger flat areas and interstep distances up to about 60 nm could be obtained; this may possibly be caused by surface decomposition to partially liquid (eutectic) phases. Thus, liquid-enhanced surface migration may explain the flattening and the increased lateral distances between growth steps.

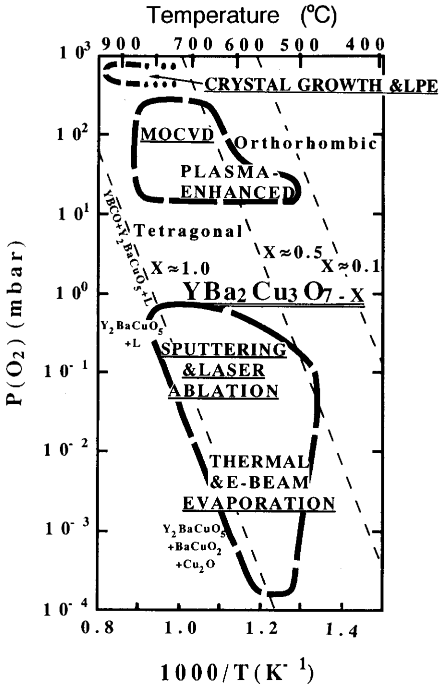

Figure 4. Stability ranges of tetragonal and orthorhombic YBCO as a function of oxygen partial pressure and temperature. The typical growth conditions of epitaxial techniques and for crystal growth are indicated.[3]

The stability relations of YBCO are actually more complex than shown in Figure 4. From high-pressure investigations one could assume that at low temperatures the 123-phase decomposes to the 124 + 211 + 023, as critically discussed in Reference 6, whereas theoretically a spinodal decomposition of YBCO into two orthorhombic phases with different oxygen ordering structures was predicted. This is an interesting field for further investigations and clarifications.

Phase Diagrams, Primary Crystallization Fields, Solubility Curves

A detailed knowledge of the phase relations is beneficial for the development of high-purity HTSC powders and ceramics, and it is essential for achieving optimum conditions for crystal growth and for liquid-phase epitaxy and for the discussion of segregation problems. However, due to the following reasons the determination of reliable phase relations is very difficult:[7] (1) The complexity of the ternary or multinary systems, (2) the valency change of Cu and the very slow equilibration of the investigated sample with the external oxygen partial pressure (causing the formation and reactions of nonequilibrium phases), (3) the sluggish reactions typical for peritectic systems and for large melting-point differences of constituent oxides, and (4) corrosion of all commercial crucibles (see next section). These difficulties and the lack of experience with complex oxide systems involving valency changes, lead to discrepancies between published phase relations. This may be demonstrated with Figure 5, which shows the primary crystallization fields (PCF) of YBCO from six different publications.[7] The establishment of definitive phase diagrams will require years of systematic efforts and collaboration. As a basis for discussion,[8] Figure 6 presents a tentative primary crystallization field of YBCO that is similar to one of the earlier published fields.[9] The PCF lies between the composition of YBCO and the eutectic between $BaCuO_2$-CuO which was established at 29 ± 1.5 mol% BaO / 910 ± 10°C in air and at 33 ± 3 mol% and 930 ± 10°C in an oxygen atmosphere.[10,11] In the literature, eutectic compositions between 18 and 40 mol% BaO have been reported. For planning and optimization of crystal growth and LPE experiments the solubility curves are essential and they are given for YBCO and NdBCO in Reference 10.

The knowledge of the phase relations is also useful for the fabrication of high-purity YBCO powder and ceramics. Very small fractions of impurities or of secondary phases may cause percolation problems, depending on the distribution as either films surrounding the superconductor grains, or as bulk inclusions with minimum interconnection. Due to the extremely short coherence lengths of the HTSC compounds, typically 0.5 to 2 nm, the corresponding thin nonsuperconducting barriers or microcracks cause severe reductions in the superconducting current density. The effect on T_c and on other superconducting properties of adding 0.36 to 1.2 wt.% CuO, $BaCO_3$, and Y_2O_3 to stoichiometric YBCO is dramatic,[12] so that it is understood now that the cation ratio has to be adjusted with high accuracy. This is not trivial since many chemicals rated as high purity (for instance 5N = 99.999%) contain large amounts of humidity or organic materials, because the nominated (N) purity refers to metallic impurities. Therefore, chemicals should be annealed to remove volatiles before weighing, and in certain cases the chemical analysis for the cation content (Ba in BaO_2 which contains BaO, hydroxide, carbonate, and often also Sr) is necessary. High-sensitivity[13] x-ray powder diffraction (detection limit 0.2 to 0.5%) is proposed to check the phases and impurities of the starting chemicals, and also to detect traces of secondary phases during synthesis. Submicron particles of the high-melting oxides and of the carbonates (Y_2O_3, $BaCO_3$) and extended liquid-assisted ball milling and optimized temperature programs in a well-controlled atmosphere are required to achieve a full reaction in one step; otherwise, annealing of precipitates from solutions containing precisely controlled cation concentrations can yield single-phase YBCO powder.

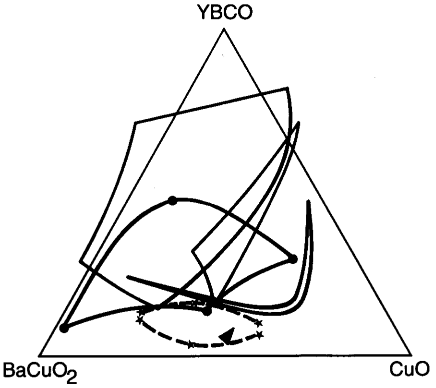

Figure 5. The primary crystallization fields (PCF) of YBCO in the ternary system $BaCuO_2$-CuO-YBCO from different authors, in molar composition.[7]

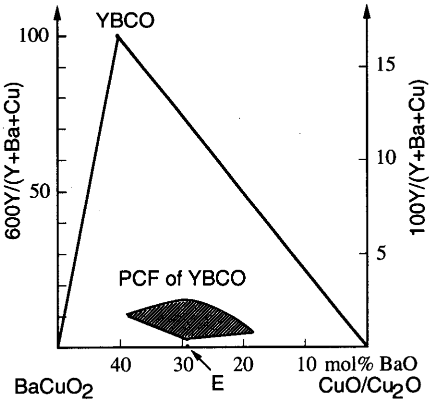

Figure 6. The eutectic composition E of the binary system $BaCuO_2$-CuO/Cu_2O and the primary crystallization field of YBCO.[8]

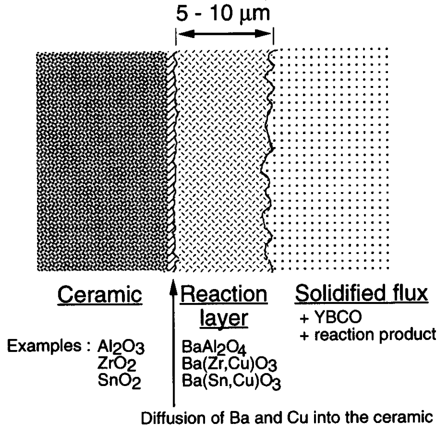

Figure 7. Schematic view of the corrosion mechanism of alumina, zirconia, and SnO_2 crucibles (from Reference 17).

Crucible Corrosion and Crucible Development

Crucible corrosion was early recognized as a problem in synthesis of HTSC compounds and crystals. Noble-metal crucibles, especially of platinum, are commonly used in crystal growth and LPE of oxide compounds.[14] However, Pt crucibles heavily corrode and cause crystallization of platinum-rich YBaCu-oxide phases[15] which are not superconducting. Gold is wetted so strongly that the liquids creep out of the crucible, an effect which was used to separate grown crystals from residual flux.[16] For YBCO, therefore, ceramic crucibles are preferable. Ceramic crucibles also corrode, but have longer lifetimes than Pt crucibles. A systematic study[17] revealed that commercial ceramic crucibles show the corrosion mechanism schematically demonstrated in Figure 7. At temperatures around 1000°C, first Ba and Cu diffuse into the ceramic, then a reaction layer a few microns thickness is formed and then dissolved, contaminating YBCO crystals (increasing the oxidation problems, and decreasing T_c) and often leading to the formation of undesired and disturbing crystals (Ba- and Y-Ba-aluminates). Therefore, overcoming the crucible-corrosion problem required either crucible-free technologies[18] or the development of corrosion-resistant crucibles. As a first stage to development of yttria crucibles, plasma-sprayed Y_2O_3 layers were studied for corrosion resistance and compared with alumina.[19] Yttria crucibles are now used for contamination-free growth and LPE of YBCO,[10,20] and are commercially available.[21] Yttria layers or substrates are investigated for textured solidification of YBCO so that the chemical interactions of $BaCuO_2$-CuO melts with yttria are of interest.[22] A specific problem for crystal growth and LPE of YBCO from yttria crucibles is the control of supersaturation and spontaneous nucleation due to the continuous dissolution of yttria.

An alternative way to reduce the contamination uses economic alumina crucibles with a flux composition (BaO:CuO ratio) optimized to control the corrosion rate and the distribution coefficient of aluminum in YBCO single crystals.[23] This way, YBCO crystals up to 4 mm lateral size and 2 mm thick could be obtained which showed a narrow T_c (<1 K) above 90 K.

Specific Aspects of the Crystal Growth of YBCO

The following section reviews the problem of separating the crystals from the flux, the recognition of thin plates as a form of growth instability leading to the achievement of bulk crystals of YBCO, and oxidation problems.

Initial crystals—important for the first physical investigations—were obtained by cooling a solid-liquid mixture containing the constituent oxides. Some investigators recovered small YBCO platelets from accidentally formed cavities,[24] whereas other groups used dental drills to obtain crystal fragments from the solidified slurry. These early investigations[25] did not follow the fundamental rules of crystal growth to achieve single-phase clean solutions and to control nucleation. However, as early as the 1987 MRS Fall Meeting the achievement of solutions of YBCO, and the decanting of the residual solutions from large crystals grown from the crucible walls were reported.[25,26] The problem with decanting is dynamic wetting, i.e., the deviation from equilibrium wetting, leading to flux droplets remaining on the crystal surface. In the "slurry method," the crystals could be slowly withdrawn from the flux by creeping along a gold foil as mentioned in the previous section.[16] In growth from bulk high-temperature solutions, the flux was slowly removed from the crystals by suction with a porous ceramic which was dipped into the solution after growth finished.[27] The best method to grow large YBCO crystals perhaps is top-seeded solution growth (TSSG),[14] which has led to one-inch crystals with inclusions and large-angle grain boundaries[28] and to 5 mm inclusion-free crystals.[29] However, the growth of large, perfect YBCO crystals is meaningless if the cracking due to oxidation and phase transition cannot be prevented, as will be discussed.

Thin platelets were generally formed in the early phase of YBCO crystallization, typical thicknesses being 10 to 100 μm and lateral dimensions up to about 3 mm. From the crystallographic structure of YBCO with a certain layer character along (001), but still with strong bonds parallel to [001], one would assume a nearly equidimensional shape as equilibrium habitus. In early 1988 the formation of thin platelets was explained by morphological instability, as a form of unstable growth corresponding to dendrites.[15] The question then was how such thin plates, frequently of high structural perfection, could grow under unstable conditions. Earlier theories of thin-plate growth were based on the twin-plane reentrant-edge mechanism or on a large number of screw dislocations causing preferential growth by Frank's spiral growth mechanism (Reference 14, Chapters 4 and 5). The answer was found when a combined SEM plus STM instrument revealed leading edges and secondary edges on the narrow side faces[30] which act like elongated dendrite tips. This leading-edge growth mechanism explains fast growth of thin plates under unstable growth conditions. On the other hand, stable growth near equilibrium at very low cooling rates, can produce thick nearly isometric crystals corresponding to the equilibrium habit. Figure 8 shows the thickness of YBCO crystals as a function of the cooling rate.[31]

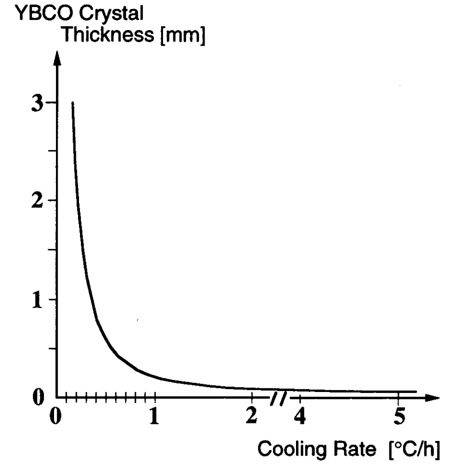

Figure 8. The influence of the cooling rate on the thickness of YBCO crystals.

Oxidation without crack formation is now the limiting factor for achieving large high-quality superconducting YBCO crystals and single-crystalline LPE-grown YBCO layers. We remember that tetragonal $YBa_2Cu_3O_{7-x}$ with $x \approx 0.8$ is grown at high temperatures and has to be oxidized to the superconducting YBCO with $x \approx 0$ to 0.1. By cooling in combination with oxidation, YBCO undergoes the transition to the orthorhombic superconducting phase at around 650°C. The splitting of the tetragonal a axes to the orthorhombic a and b axes (see next section on epitaxy) as well as the transition-induced change of the c lattice parameter lead to strain which for small crystals can be relieved by twin formation. However, with increasing crystal and layer size and crystalline perfection, cracking is observed to relieve excessive strain. This problem is enhanced by extremely slow oxidation kinetics (requiring lengthy experiments) and by significant anisotropy of the oxygen diffusion coefficients found not only in the directions parallel and perpendicular to the layer ($\sim 10^6$), but even within the layer ($\sim 10^2$).[32] The oxidation is further hampered by contamination of YBCO, for instance from the alumina crucibles. Solving this problem by systematic experiments would require excessive time and would destroy numerous high-quality crystals and layers. Therefore, a theoretical approach is necessary which, however, is quite complex and which requires reliable data on the temperature and anisotropy dependence of diffusion, the lattice constants, and the mechanical properties of YBCO. Perhaps the problem can be somewhat reduced by changing from the popular YBCO to NdBCO or LaBCO, which have much smaller orthorhombicities, i.e., smaller differences between the orthorhombic a and b axes.

Materials Engineering Problems in Epitaxy of High T_c Superconductors

For the development of HTSC tunnel-device technology, specifically for digital applications and for SQUIDs, compact homogeneous layers and multilayer structures with very flat surfaces are required. In view of the short coherence lengths of cuprate superconductors, only smooth surfaces on structurally "perfect" layers allow planar technology, reproducible etching structures, and the small spreads of the device characteristics. Expected high yields in device fabrication are an additional advantage of flat perfect layers. Despite large efforts in initially about 1,000 groups working in PVD (sputtering, pulsed-laser deposition, MBE, etc.), about 30 groups working in MOCVD, and about 10 groups worldwide working on LPE, such surface flatness could not be achieved. Only very recently the first single-crystalline YBCO layers with quite flat surfaces have been achieved by LPE.[10,33] The critical factors determining perfection and surface morphology, i.e., the nucleation and growth modes in epitaxy, will be briefly described[34] as well as the major problems in HTSC epitaxy.[3]

The most important factors determining nucleation and growth modes are the supersaturation σ and the chemical potential, respectively, as the driving forces for epitaxy. The supersaturation factor can be expressed in terms of the concentration relations in the gaseous, liquid, and solid states, or by the relative supersaturation,

$$\sigma = \frac{n - n_e}{n_e} = \frac{\Phi \Delta T}{RT^2}$$

with n and n_e the actual and the equilibrium concentrations, Φ the molar heat of solution, ΔT the undercooling, and R and T the gas constant and the absolute temperature, respectively. The comparison of PVD, CVD, and LPE techniques is straightforward by using the respective Gibbs free energy differences ΔG between reactants and products at the growth temperature. For PVD and CVD, ΔG is about 600 kcal/mol; in LPE, ΔG values are about 30–50 cal/mol, which is more than four orders of magnitude lower than in vapor growth.[34] These great differences lead to two-dimensional nucleation and localized step propagation in PVD and CVD, and to spiral growth and propagation of steps over macroscopic distances in LPE. The lateral distances between steps reflect the supersaturation differences: 20–50 nm in vapor growth, and 0.5–10 μm in LPE.[34]

The misfit between the substrate and the YBCO layer at the epitaxial growth temperature also strongly influences the surface nucleation and growth modes. Misfit reduces the step-flow regime (layer-by-layer growth) and enhances two-dimensional nucleation (island formation).[34] Thus the misfit acts in the same direction as high supersaturation, and the supersaturation required for growth increases with higher misfit. The effect of misfit on the growth mode[35] is shown in Figure 9. Most substrates used in PVD and CVD have more than 0.1 or even more than 0.5% misfit so that the layer-by-layer growth mode over macroscopic distances is excluded except when large substrate misorientations are used. When the distances between the misorientation steps are less than about 19 r_s (r_s being the size of the critical surface nucleus), then two-dimensional nucleation can be suppressed in favor of a very high step density.[34] The critical layer thickness, as a function of misfit, for crack propagation is shown in Figure 9.[34,35] The strain caused by misfit and by cooling due to thermal expansion differences may be partially or completely relaxed by the formation of misfit dislocations, by microcracks, or by macroscopic cracks, depending on the elastic strain accommodation and on the oxidation/phase transition-induced strains discussed in the previous section. All these features affect the superconducting properties, especially flux pinning and the critical current density and its field dependence. It is astonishing that these materials engineering problems have received little attention so far. A schematic of the combined effect of supersaturation and misfit is shown in Figure 10. Only at very low supersaturation (by liquid-phase epitaxy) using low-misfit substrates can really flat YBCO layers—as required for tunnel-device technology—be expected.[34]

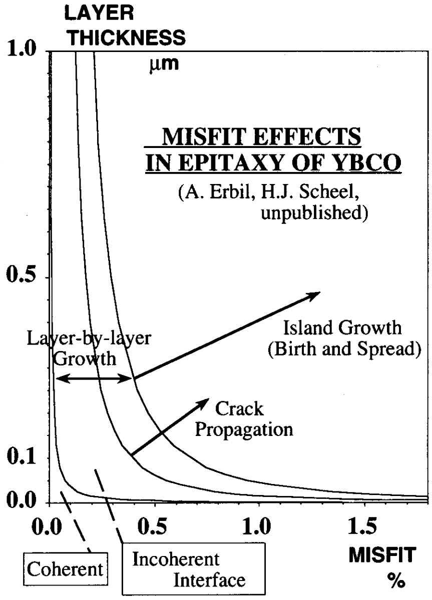

Figure 9. The effect of substrate misfit on the growth mode, the interface structure, and crack propagation as a function of layer thickness.[34,35]

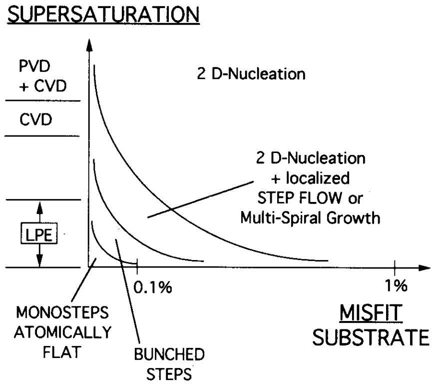

Figure 10. Schematic of the combined effect of supersaturation and misfit on the growth mode and step structures.[34]

Surface morphological studies are important for evaluating growth modes and optimizing epitaxial processes. The most powerful tools are the scanning tunneling microscope (STM) and related techniques for vapor-grown surfaces, and the Nomarski differential interference contrast microscope (DIM) for LPE-grown surfaces with large interstep distances. Figure 11 shows the detection limits of the most important microscope techniques along with observed step heights and interstep distances of PVD-, CVD-, and LPE-grown YBCO layers. Also shown are the inherent limits of PVD processes and the practical limits of LPE interstep distances.

The origin of the macroscopic growth spirals in crystal growth from high-temperature solutions was found to be screw dislocations,[14] and Burton, Cabrera and Frank derived the classical BCF growth theory. In contrast, the occurrence of the large number of spiral islands (3×10^8 to $> 10^9$ per cm^2) in PVD and CVD is not yet clarified. The spiral density, however, corresponds to the number of two-dimensional nuclei, so that a model based on coalescence of slightly tilted growth islands[34,37] has a high probability of being correct. In Figure 12 the submicroscopically small spiral islands typical for epitaxial deposition from the vapor phase are shown and compared with the macroscopic growth spirals obtained by LPE.[33] The distances between growth steps are 26 nm and 0.6 μm, respectively. The largest interstep distance achieved so far (17 μm) was also obtained by LPE.[10]

Substrates play a significant role in the development of epitaxy of YBCO and of other high T_c compounds. In addition to misfit, misorientation, and thermal expansion already discussed, substrates should fulfill other requirements: chemical and thermal stability, lack of structural phase transitions causing twinning (thus excluding most perovskites), specific dielectric and microwave properties depending on the applications, mechanical strength, and economic fabricability and machinability. Since substrates with such properties have not been developed yet, an alternative approach consists of buffer layers on low-cost substrates like silicon or sapphire, or on polycrystalline substrates like steel. Still another alternative is graphoepitaxy, i.e., substrates with artificial surface structures like grooves, or with "structural graphoepitaxy" where the substrate surface has regular corrugations due to the crystallographic structure, which control the epitaxial orientation of the high T_c superconductors.[38]

Figure 13 shows some of the widely used substrates and the temperature dependence of their lattice constants. Also shown

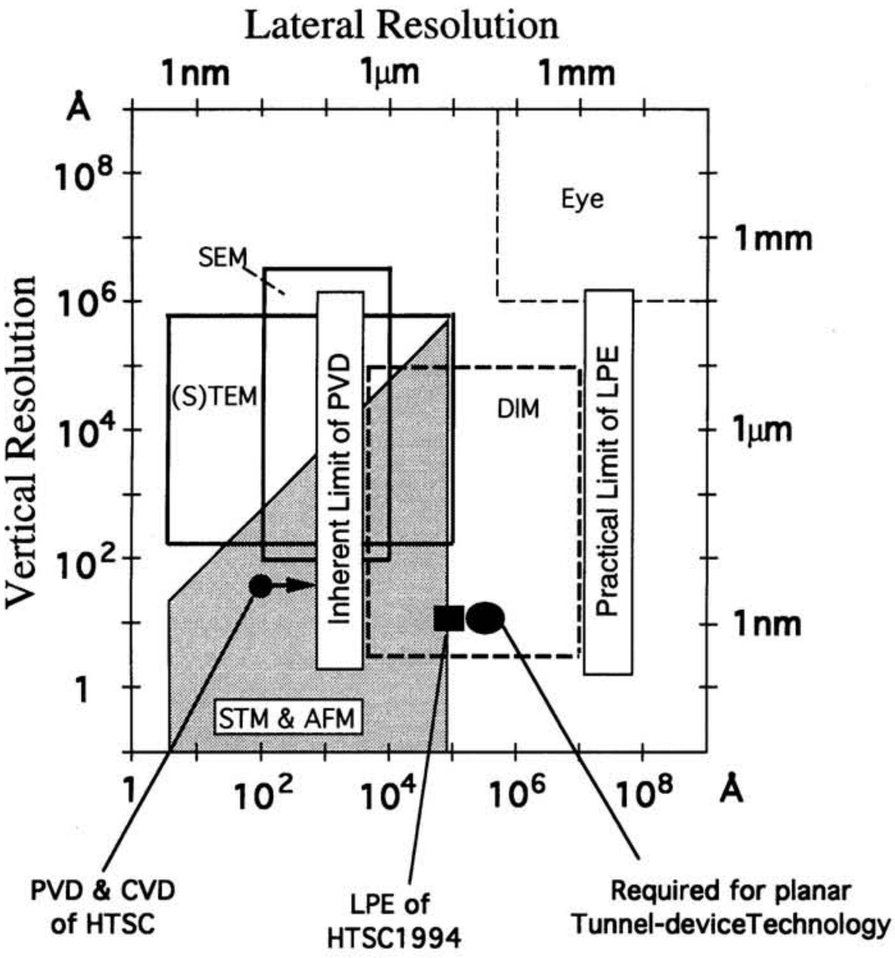

Figure 11. Surfaces (step heights and lateral step distances) of YBCO grown by PVD, CVD, and LPE and the detection limits of electron microscopes (SEM, TEM), scanning tunneling microscopy (STM) and atomic force microscopy (AFM), and of the optical differential interference contrast (Nomarski) microscope (DIM). Also shown are the inherent limit of PVD and the practical limit of LPE by vertical bars, and the step distances required for a planar HTSC tunnel-device technology.[34]

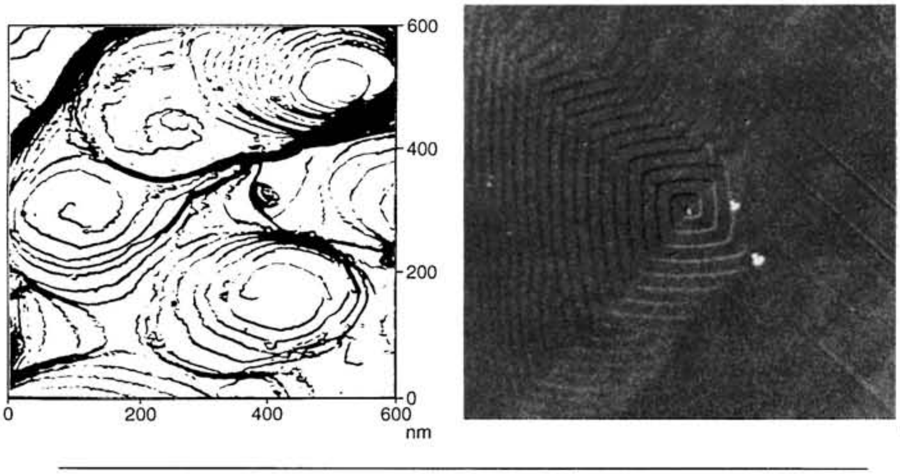

Figure 12. Typical spiral structures of (a) CVD-grown[36] *and (b) LPE-grown YBCO layers. The LPE spiral has a diameter of 62 μm. Note the different scales which correspond to >3 × 10^8 spiral islands/cm^2 in vapor-grown and to about 10^3 spirals/cm^2 in LPE-grown layers.*

is YBCO with the tetragonal-orthorhombic phase transition. The tolerance of misfit at the epitaxial growth temperature is less than 0.1%, and the thermal expansion difference between the HTSC layer and the substrate should be smaller than 20%.[35] None of the substrates fulfills these conditions; on the contrary, misfit is nearly always larger than 1% so that in principle[39] flat surfaces and layer-by-layer growth over macroscopic distances cannot be expected.[34] Another problem, twinning due to strain relaxation in connection with structural phase transitions, is quite common in perovskites. Twinning in $LaGaO_3$, for instance, leads to surface corrugations and to reduced critical current densities.[40] Applying uniaxial pressure and passing through the phase transition (T_c of $LaGaO_3$ is 149–151°C) produced single-domain substrates of 1 cm^2.[41] An alternative approach to circumvent twinning is the development of nonperovskite substrates, for instance of the K_2NiF_4 structure.[42] There is hope that development of an optimized substrate and optimum growth and oxidation procedures, will allow single-domain crack-free HTSC layers with atomically flat surfaces, but this requires intensive efforts to solve complex materials engineering problems. In comparison, the measurement of superconducting properties (T_c, $J_c(H,T)$) seems quite routine.

Characterization

The complexity of high T_c cuprate compositions and structure (including different oxygen sites and site occupancies) excludes reproducible preparation of crystals and layers. Ten or more growth parameters influence the properties of the crystalline product, and the majority of the growth parameters cannot be controlled with sufficient accuracy. Even "simple" silicon crystals mass produced in the same Czochralski puller by the same person have to be characterized before use. Since exact replication is not possible, the crystals and layers have to be sufficiently characterized in order to reproduce the specific physical properties or functions. Sufficient characterization[3] (in contrast to no and to complete characterization) consists of the analysis of only those chemical and structural aspects of the sample which have an impact or which may have an impact on the specific physical measurement or application. Such characterization requires considerable effort and multidisciplinary collaborations. But sufficient characterization would assist with the interpretation of physical measurements, and thus would lead to accelerated progress in HTSC science and technology.

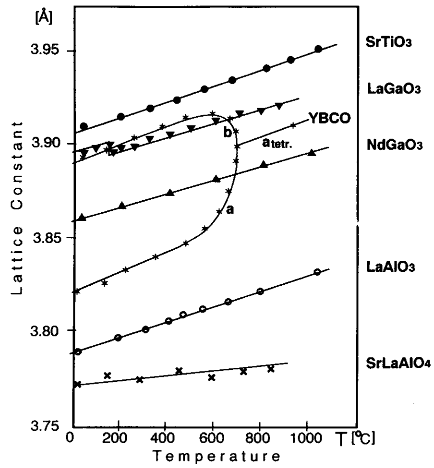

Figure 13. Lattice constants and thermal expansion of YBCO and a few important substrates. MgO and ZrO_2 are out of scale, MgO with a lattice constant of 4.21 Å at the top and ZrO_2:Y with a lattice constant of 3.63 $\sqrt{2}$ Å at the bottom of the figure.

Conclusions

The discovery of superconductivity above the boiling point of nitrogen has confronted materials scientists and technologists with a broad spectrum of fascinating and complex problems. The complexity of materials problems of cuprate superconductors requires the collaboration of solid-state chemists, materials engineers, crystallographers, and crystal growth experts. The great initial promises and forecasts are yet to be realized, but through carefully directed research, many opportunities lie ahead.

This review has described a few important materials problems in the crystal growth and epitaxy of YBCO as a representative of the 123 compounds. There are similar problems and needs in the development of wires, coils, bearings for levitation, etc. In the other major classes of high T_c superconductors (Bi-, Tl-, and Hg-based cuprates) most of these materials problems are even greater. For instance, the PCFs of compounds with the highest T_c are not yet established and are expected to be extremely narrow. This aspect, in combination with the plurality of compounds with similar compositions and similar lateral lattice constants, causes the "chemical polytypism." This is an ordered (epitaxial) stacking of layer sequences with different compositions. Therefore, to achieve a breakthrough in HTSC applications, it is necessary to develop HTSC compounds with reduced materials problems, or to solve the materials engineering problems of the present most promising compound.

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