

MBE SYNTHESIS OF $\text{YBa}_2\text{Cu}_3\text{O}_y$ SUPERCONDUCTING THIN FILMS

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Abstract-- We discuss issues concerning molecular beam epitaxy of the superconductor $\text{YBa}_2\text{Cu}_3\text{O}_y$. We have made films by MBE at low pressures using molecular oxygen and ozone. A minimum incidence rate of each of these species for synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_y$ is established and compared with the thermodynamic stability data and lower kinetic limits. For ozone the lower limit appears to be determined by the growth rate. Generally the best films that are made at low pressures (less than 10^{-2} mbar of oxygen or with ozone) have slightly lower transition temperatures and expanded c-axes, but still sharp transitions and high critical currents. Cation disorder is suggested as a likely explanation for these properties. We discuss the model of solubility of Ba on the Y sites and find it consistent with experimental results.

I. INTRODUCTION

Molecular beam epitaxy (MBE) is physical vapor deposition by use of molecular or atomic beams at very low levels of supersaturation. MBE has gained a reputation for growth of excellent quality crystalline semiconductors, in particular the III-V systems such as GaAs. More recently the MBE technique has been applied to thin film growth of the cuprate superconductors. For the cuprates, which are naturally layered materials, the precise compositional control of an MBE deposition system could offer the possibility of designing the material on a unit cell level. Since the variety of physical properties of the cuprates is very rich, including metallic, semiconducting, and superconducting behavior, the materials design can offer a unique integration of various physical phenomena. This assumes that one can achieve sufficient control over growth and design of the material. Although many groups have successfully made cuprate films, much still remains to be learned about the structure of these materials. In particular their defect structures are not well known, although important for superconductivity with a coherence length which is of a unit cell size.

In this paper we review some of the still outstanding challenges in growth of cuprates, focussing on the best known cuprate system, $\text{YBa}_2\text{Cu}_3\text{O}_y$. We address two of the main issues in MBE growth of cuprates, oxygen stability and issue of activated species, and thermodynamic and kinetic issues in the phase diagram at lower oxygen pressure and temperature.

II. DEPOSITION CHAMBER

The Delft deposition chamber is equipped with 2 electron-guns and 4 Knudsen-cell sources [1]. Y and Cu are evaporated from the e-guns, and Ba from a K-cell. A key issue in such a multi-source system for deposition of cuprates is stability of the evaporation rates. A feedback system utilizing independent and differentially pumped mass spectrometers is used for each of the e-guns. The feedback system we use produces rate

stability to within 1-2% per hour as determined by an independent measurement on a quartz crystal microbalance [1]. K-cells are kept at constant temperature and their rates fluctuate 2-3% per hour, for the deposition rates used here. The e-guns can only operate well if the pressure at the guns is kept at less than 5×10^{-4} mbar. However, because the mass spectrometer feedback for the e-guns is very sensitive to system pressure above $\sim 10^{-5}$ mbar, it is preferable to keep the system pressure below 10^{-5} mbar. The deposition rate used in our study is 0.1-0.2 nm/s of $\text{YBa}_2\text{Cu}_3\text{O}_y$.

The deposition system consists of two parts, the lower part where the sources are and the upper part where deposition occurs and sources are monitored. The two are separated by a liquid nitrogen shroud with suitable openings for the source materials to be evaporated on the sample and mass spectrometers. The sources are pumped with a 500 ℓ/s turbo pump. Oxygen and ozone are brought in through a tube whose outlet is 4-7 cm away from the substrate. The upper part of the chamber is pumped by a 2200 ℓ/s turbo pump mounted on top of the system. In this way most of the oxygen/ozone is pumped away directly at the top, maintaining a low pressure at the sources. The total pumping speed at the sample position is approximately 1500 ℓ/s . Such a high pumping speed is desirable in order to obtain a low pressure in the system which is needed for good rate control, while at the same time being able to introduce high flow rates of ozone near the substrate.

Ozone is produced by a commercial silent discharge generator, which produces approximately 5% ozone in a mixture with oxygen. Ozone is condensed and distilled at a temperature of about 140K. Enough ozone is produced in 10 minutes for several hours of deposition. After condensing the ozone, the still is pumped out and then the ozone is evaporated slowly into the deposition chamber. Typical ozone flow rates in the system are 0.01-0.05 mbar $\cdot\ell/\text{s}$. In tests by recondensing the ozone, we have determined that the purity of the ozone beam is at least above 50% (less than half of the ozone dissociates before reaching the sample). For the purposes of the discussion here, we will assume 100% purity.

III. MINIMUM OXYGEN REQUIREMENT

A. Thermodynamic and Kinetic Oxygen Requirements

Cuprates are oxide materials. Because of that fact a certain chemical potential of oxygen needs to be applied to the material so that it does not decompose to other phases, which require less (or more) oxygen. Practically, this thermodynamic requirement means that the superconducting cuprate materials will only be stable in a certain portion of oxygen pressure-temperature phase space.

Figure 1 shows the part of the pO_2 -T phase space where $\text{YBa}_2\text{Cu}_3\text{O}_y$ is thermodynamically stable below atmospheric

pressures of oxygen, as presently understood from thermodynamic studies. The main features of the thermodynamic studies are the melting-decomposition line, m_1 , relevant at higher oxygen pressures, and a solid-state decomposition line at lower pressures, d_1 . There appears to be still some disagreement on the position of d_1 between the various studies [2,3]. We will use the data of Lindemer et al. [3]. The $\text{YBa}_2\text{Cu}_3\text{O}_y$ phase is stable to the right of m_1 and d_1 and to the left of d_2 .

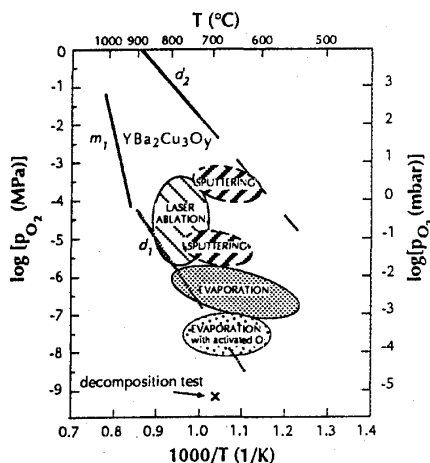


Fig. 1. Thermodynamic stability lines for $\text{YBa}_2\text{Cu}_3\text{O}_y$, as reported in the literature and extrapolated to lower pressures (dashed lines). Shaded regions represent in-situ growth regimes.

The thermodynamic studies are performed on bulk samples. It is not a priori obvious whether such studies are important for thin film growth where one can in principle form metastable phases. However, Hammond and Bormann [4] first proposed the relevance of the stability line for in-situ growth of cuprates. Because of the relatively high deposition temperatures compared to the melting temperature (0.8-0.9 T_m) kinetics may not be very limiting. Figure 1 also shows the regions of phase space where $\text{YBa}_2\text{Cu}_3\text{O}_y$ thin films have been grown successfully by different techniques. One can see that the regions corresponding to synthesis with molecular oxygen lie in the part of the diagram where $\text{YBa}_2\text{Cu}_3\text{O}_y$ is thermodynamically stable, as judged by extrapolating the thermodynamic lines to lower pressures and temperatures. This is in agreement with the expectation that one should be able to crystallize $\text{YBa}_2\text{Cu}_3\text{O}_y$ only where it is the lowest energy state. The trend, however is that the best films, in terms of T_c and crystalline quality, are made close to the line d_1 [4].

In MBE synthesis one would like to work in a pressure regime below 10^{-5} mbar. In order to circumvent the thermodynamic limitations of molecular oxygen, many researchers have utilized activated species of oxygen, such as O or O_3 . These have a free energy higher than O_2 and therefore will more readily oxidize the metal atoms. Naturally, these activated species cannot be in thermodynamic equilibrium (otherwise O_2 would form), so it is not clear how relevant a thermodynamic comparison is. Nevertheless, if one compares the decomposition line d_1 for O_3 to the one for O_2 (i.e. use

O_3 instead of O_2 in the decomposition reaction), the line would be outside of Fig. 1 to the left, i.e. $\text{YBa}_2\text{Cu}_3\text{O}_y$ would be stable at all practical pressures and temperatures during deposition; see also Ref. [5]. This would mean that d_1 is not a limitation for making films with ozone. Eventually, at higher temperature and/or lower pressure one is limited by the melting line (extrapolation of a line m_1). We have done tests to verify the stability of the $\text{YBa}_2\text{Cu}_3\text{O}_y$ below the line d_1 in the presence of ozone. Films of $\text{YBa}_2\text{Cu}_3\text{O}_y$ made by laser ablation, were introduced in our MBE system and heated to 690°C for one hour. We found no indications for decomposition at the point marked with a cross in Fig. 1, in the presence of an incidence rate of 10^{14} ozone molecules/ cm^2s . This is an ozone partial pressure of 4×10^{-7} , in addition to the oxygen pressure of about 10^{-5} mbar. For the same treatment in just molecular oxygen (i.e. without ozone) the $\text{YBa}_2\text{Cu}_3\text{O}_y$ decomposed.

We also consider here the lower kinetic limitation due to the need of 6 O atoms per growth of one $\text{YBa}_2\text{Cu}_3\text{O}_6$ unit cell. First we consider the ozone species. Assuming each O_3 molecule gives one O atom, this limit translates to an incidence rate of 7×10^{14} molec/ cm^2sec , or an ozone partial pressure of 3×10^{-6} mbar, for our deposition rate of 0.2 nm/s. In practice one has to deal with an impinging flux of ozone and a somewhat higher background pressure of predominantly oxygen molecules. The ratio of these two will depend on the ozone delivery set-up and the pumping speed of the system. However, the relevance here is that some of the oxygen for a unit cell could also be obtained from oxygen molecules.

For molecular oxygen, one can set an absolute lower limit obtained by assuming that both O atoms of every molecule which impinges on the growth surface are incorporated in the structure. This limit translates to 3.4×10^{14} molecules/ cm^2s for 0.2 nm/s, or a pressure of 1.3×10^{-6} mbar. Equivalently, one can get the maximum number of O atoms available for growth of a unit cell from a pressure of oxygen p at a deposition rate r as

$$N_{\text{maxO}} = 9.5 \times 10^5 \frac{p \text{ (mbar)}}{r \text{ (nm/s)}}$$

The kinetic limit due to growth then states that this number be equal to 6. This limit is certainly not valid at the deposition temperatures in question, but it gives a good idea of how many oxygens are available. At 5×10^{-4} mbar about 3000 O atoms are available per unit cell for a rate of 0.2 nm/s.

B. Film synthesis

We have made films of $\text{YBa}_2\text{Cu}_3\text{O}_y$ at various oxygen conditions in order to establish lower limits on pressure requirements. The temperature during deposition was $650\text{--}700^\circ\text{C}$, the rate of deposition about 0.2 nm/s, and the composition kept close to the 1:2:3 stoichiometry. For molecular oxygen we were not able to make $\text{YBa}_2\text{Cu}_3\text{O}_y$ films below 5×10^{-4} mbar. This means that the lower limit is above our maximum operating pressure. From other work, Ref. [6], we know that the limit is just below 10^{-3} mbar. This compares rather well with the thermodynamic decomposition line d_1 of Fig. 1, although it is a bit above the line. Kinetics of oxygen reaction may be causing the slight disagreement.

For ozone, we find the lower limit to make $\text{YBa}_2\text{Cu}_3\text{O}_y$ in the range of $2\text{--}8 \times 10^{14}$ ozone molecules/ cm^2s , at a background pressure of $\sim 2 \times 10^{-5}$ mbar [1]. As stated already, the background pressure, which is due to finite pumping speed, is presumed to be mostly oxygen, since most of the ozone will dissociate when striking the hot substrate block. At these pressures the number of O atoms supplied by the ozone flux is between 2 and 10 per growth of one unit cell, agreeing with the expected kinetic limit of about 6. Therefore it appears likely that the lower limit for the ozone flux is defined by growth requirements. This is also consistent with the results of Kubinski et al [5], who find the lower limit for ozone to be about 3 molecules per unit cell. They suggest that the other 3 O atoms for the unit cell are supplied by the molecular oxygen background pressure.

At the lowest pressures where one can make $\text{YBa}_2\text{Cu}_3\text{O}_y$ films, it has been reported that excess Y during growth stabilizes the "123" phase [7,8]. Thus, the actual lower limit necessary for growth also depends on the composition.

C. Discussion of minimum pressure

In order to work at the lowest possible pressures in an MBE system one has to utilize activated species of oxygen, such as ozone. In that case, if one has a sufficiently high pumping speed, it is rather easy to achieve pressures $< 10^{-5}$ mbar in the system during synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_y$. Furthermore, from the considerations mentioned above, it appears that the pressure limitation for ozone is purely kinetic due to growth rate. If this is true, then one should be able to go to even lower incidence rates and pressures during growth, by reducing the deposition rate. As far as we are aware this has not been tested in detail. Lower deposition rates, or lower supersaturation, would also approach more equilibrium conditions, which would be particularly beneficial for MBE.

The above discussion for ozone should be similar for other activated species such as atomic oxygen. The only advantage of ozone, as we see it, is purely technological, i.e. the ease of preparing almost pure ozone jets.

IV. FILMS MADE AT LOW PRESSURES

A. Expanded c-axis

Films which we have made at the lowest necessary ozone pressures have in the best cases T_c 's by a few degrees lower than the 92K bulk value and a much expanded c-axes over what would be expected for the corresponding chain oxygen content reduction. This has been discussed at length in Ref. [6]. Our resistive transitions in the best cases are less than 2 degrees wide and J_c is above 10^6 A/ cm^2 at 80K.

The dilated c-axis is a ubiquitous feature of in-situ films grown at lower pressures of oxygen. Figure 2 shows the dependence of the c-axis lattice parameter on growth pressure, as reported in Refs. [6,9,10,11] for evaporation, sputtering and laser ablation.

B. Possible changes in the phase diagram at low pressures

As has been argued in Ref. [6] cation disorder appears to be the only acceptable explanation for the anomalous properties

of films synthesized at low pressures of oxygen. More recently Feenstra et al. [12] have shown that the films made at lower pressures are hole-doped compared to the bulk $\text{YBa}_2\text{Cu}_3\text{O}_y$. This behavior is very similar to the one observed when one intentionally dopes $\text{YBa}_2\text{Cu}_3\text{O}_y$ with Ca. As discussed in Ref. [13] this suggests that Ba, which is divalent as is Ca, could be partially substituting for the trivalent Y at lower pressures. The mechanism suggested is based on charge compensation: Ba^{2+} is favored over Y^{3+} at lower pressures of oxygen. Thus there should be cation solubility in the Y layer, with Ba increasingly substituting Y at lower pressures. In analogy with Fig. 2, we draw a proposal for the phase diagram in Fig. 3. On the other hand, at atmospheric oxygen pressures $\text{YBa}_2\text{Cu}_3\text{O}_y$ is known to be a line compound in the metal atoms, i.e. it has no cation solubility. Note that there could be the converse effect of Y substituting on the Ba sites at even higher pressures as shown in Fig. 3.

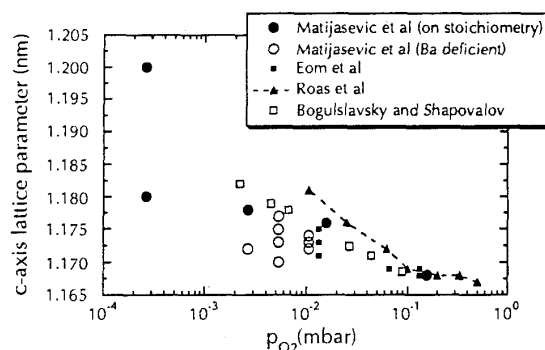


Fig. 2. Expansion of the c-axis lattice parameter as a function of oxygen pressure during growth, as reported in the literature [6,9,10,11].

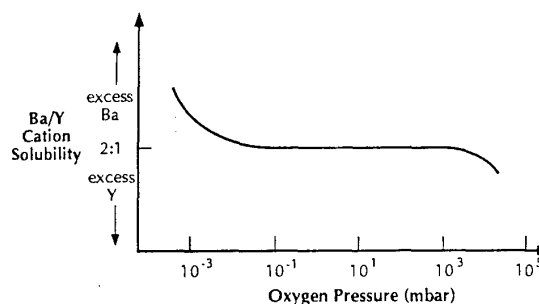


Fig. 3. Proposed solubility of the $\text{YBa}_2\text{Cu}_3\text{O}_y$ phase as a function of oxygen pressure.

It appears that Ba-for-Y substitution can explain most of the properties of best films made at low pressures, but not for all films. In particular, when the deposition temperature is reduced the T_c drops more rapidly with increasing c-axis, see for example Ref. [9], then is observed for the films with the highest T_c 's. Whether this is an 'intrinsic' effect, i.e. due to disorder in the lattice, or more extrinsic, such as disorder between grains, remains to be shown exactly.

Rare earth atoms can substitute for Y in the $\text{YBa}_2\text{Cu}_3\text{O}_y$ phase producing the same structure and a very similar

superconducting transition temperature [14]. It has been reported for bulk samples made at atmospheric oxygen pressures that Sm forms the same structure on-stoichiometry, but in contrast to $\text{YBa}_2\text{Cu}_3\text{O}_y$, also has an extended solubility of Sm on the Ba sites off-stoichiometry. The phase is reported to be $\text{Sm}_1(\text{Ba}_{2-x}\text{Sm}_x)\text{Cu}_3\text{O}_y$ [14]. Such a solubility is the one represented on the right side of Fig. 3. Preliminary work on MBE synthesis of SmBaCuO films shows that in fact this solubility does not exist at lower pressures [15], consistent with our model, assuming that for SmBaCuO the gap in solubility ranges is smaller.

However, the exact nature of the disorder has not been settled yet [7,11,13]. In order to obtain a clear picture of any existing atomic disorder, the local structure must be probed. Experimental techniques which are sensitive to the local atomic ordering should be employed to settle these questions. Understanding of the disorder and its correlation with growth parameters is important if one wants to be able to control the defects as well as to utilize doping and solubility effects in the cuprates. $\text{YBa}_2\text{Cu}_3\text{O}_y$ is the most studied material, but similar effects no doubt take place in the other cuprates.

The importance of these atomic scale defects for superconductivity comes out because of the very short coherence length in the cuprates. Atomic disorder could have important influence on pinning and critical currents [16], as well as microwave losses by increasing the quasiparticle scattering rate [17].

V. CONCLUSIONS

We have discussed the pressure requirements for synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_y$. We conclude that synthesis with molecular oxygen is limited to pressures above the stability line, if one excludes stoichiometry effects. For growth with activated species, we deduce that it must be kinetically limited. In that case lower pressure requirements should be achievable at lower deposition rates.

As discussed previously in the literature, the c-axis expansion, stoichiometry effects, and hole doping of the material all point to the conclusion that cation disorder takes place in the $\text{YBa}_2\text{Cu}_3\text{O}_y$ phase at low growth pressures. The structural changes and their mechanisms are still largely unknown. Ba-for-Y substitution induced by low chemical potential of oxygen appears to be a good model to explain some of these results, but there may be other disorder as well. Structural studies of the disorder in in-situ films are needed to settle these questions. Such atomic scale disorder is also bound to have an effect on the superconducting and other properties of the material.

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