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MOCVD Routes to $\text{Ti}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4+2n}$ Superconductor and Dielectric Insulator Thin Films

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Abstract. The evolution of HTS device technologies will benefit from the development of MOCVD (Metal-organic Chemical Vapor Deposition) routes to high quality HTS films as well as to those of insulators with low dielectric loss and close HTS lattice matches. Reviewed here are research efforts at precursor design focusing on Ba sources. A novel low pressure TGA technique is used to compare volatilities of MOCVD precursors and to quantify the role of gas phase diffusion in film growth. To form high quality $\text{Ti}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4+2n}$ ($n = 2,3$) films, $\text{BaCaCuO}(\text{F})$ films are first deposited by MOCVD using the liquid precursors $\text{Ba}(\text{hfa})_2\cdot\text{mep}$, $\text{Ca}(\text{hfa})_2\cdot\text{tet}$, and solid $\text{Cu}(\text{dpm})_2$ (hfa = hexafluoroacetylacetonate, dpm = dipivaloylmethanate, mep = methylethylpentaglyme, tet = tetraglyme). The film growth process is shown to be mass transport-limited, and an interesting ligand exchange process is identified. The superconducting TBCCO phase is formed following an ex-situ anneal in the presence of Ti_2O at temperatures from 820-900°C. Transport properties of TBCCO-2223 films include a T_c as high as 115K, J_c of $2 \times 10^5 \text{ A/cm}^2$ (77K), and R_s of $0.35 \text{ m}\Omega$ (5K, 10 GHz). The MOCVD growth of low loss, lattice-matched dielectric NdGaO_3 , PrGaO_3 , $\text{Sr}_2\text{AlTaO}_6$, and SrPrGaO_4 films is also discussed. High quality $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films have been grown upon MOCVD-derived PrGaO_3 substrates.

1. INTRODUCTION

The discovery of high temperature superconducting (HTS) oxides promises the realization of many novel thin film device concepts. Among these are Josephson junction-based devices for highly sensitive magnetic field detection or ultra-fast computation.[1] Due to the inherently low surface resistance, passive microwave devices such as filters and delay lines are other important applications of HTS materials.[2] Many of these HTS-based devices also require insulating, lattice-matched, low-loss dielectric oxide films. To fabricate such devices on a large scale, an efficient method to produce high-quality thin films of oxide superconductors and dielectrics must be developed. MOCVD has many important attractions in terms of ability to coat large areas with high throughput under highly oxidizing conditions. However, the MOCVD technique also offers many challenges. These include the synthesis and characterization of suitably volatile precursors, understanding precursor decomposition and crystal growth mechanisms, and efficient reactor design. Of particular interest here is the growth of the TiBaCaCuO family of superconductors which have among the highest known critical temperatures (125K).[3] The growth of these materials by MOCVD presents the challenge of finding a suitably volatile barium source and understanding the complex phase relationships of the TiBaCaCuO (TBCCO-

family of superconductors. Presented here are the efforts to: 1) Develop suitably volatile alkaline and rare earth precursors. 2) Characterize their volatility and vapor pressure temporal stability with a novel reduced pressure thermogravimetric analysis. 3) Characterize the MOCVD growth process for BaCaCuO(F) thin films. 4) Grow high quality $Tl_2Ba_2Ca_{n-1}Cu_nO_x$ thin films in a post annealing process and characterize transport and microwave properties. 5) Grow high quality lattice-matched dielectrics by MOCVD for use with HTS materials.

2. EXPERIMENTAL

2.1 Metal-organic precursor synthesis and TGA characterization

Ba(hfa) $_2$ •mep, Ca(hfa) $_2$ •tet, and Cu(dpm) $_2$ (hfa = hexafluoroacetylacetonate, dpm = dipivaloylmethanate, mep = methylethylpentaglyme, tet = tetraglyme) are prepared as described in the literature.[4] Ba(dpm) $_2$ is synthesized anhydrously from the reaction of Ba metal with Hdpm in THF solution. To measure the relative volatilities, sublimation rates of precursors were measured in a TA Instruments STD simultaneous thermogravimetric-differential thermal analysis (TGA-DTA) apparatus. The TGA-DTA directs a horizontal carrier gas flow across 3.4 mm deep alumina sample pans mounted on microbalance arms. Pressure is adjusted by N $_2$ flow rate (50-100 sccm) and by a throttle valve in the connection to the 14 CFM direct drive pump.

2.2 MOCVD growth

The research MOCVD reactor used in this study (Figure 1) is of a straightforward horizontal design, and details are described elsewhere.[5,6] Metal-organic precursor reservoirs are individually heated in thermostated oil baths, and carrier flows are mixed in a common manifold. To aid in uniformity of deposition rate, a quartz laminar flow chamber is utilized. The 3:1 aspect ratio of width-to-height in this flow chamber reduces thermal buoyancy effects, thus enhancing the stability of carrier flow.[7] A SiC-coated graphite susceptor is positioned at the end of the flow chamber and is angled at 8.7° to aid uniformity of deposition along the length of the substrate. The susceptor is heated by a 6 kW water-

Figure 1. Schematic of research MOCVD reactor.

cooled IR lamp, and temperature is monitored by a K-type thermocouple on the surface of the susceptor. Pressure is controlled by throttle valve. To find stoichiometry and deposition rates, the metal content of films is determined using an AtomScan 25 ICP atomic emission spectrometer. In the byproduct trapping study, a 0° C trap is placed on the bypass line 10 cm downstream from the bypass valve. A small tube furnace, at 400° C, is placed around the bypass line between the trap and bypass valve. Oxidizer is introduced at the common precursor manifold.

2.3 $Tl_2Ba_2Ca_{n-1}Cu_nO_{4+2n}$ phase formation

Due to the high volatility and extreme reactivity of Tl_2O , it is difficult to grow films in an *in-situ* process (i.e., one not requiring a post-anneal). MOCVD derived $BaCaCuO(F)$ films are thus reacted with an equilibrium pressure of Tl_2O from a bulk TBCCO superconductor pellet of maintained at temperatures between 820-900°C. The pellet is prepared from presintered Tl_2O_3 , BaO, CaO, CuO powders with cation ratios of 2212 or 2223. The film is supported face down over the pellet with gold foil and sealed in a crimped gold foil crucible to minimize Tl_2O loss. The atmosphere of the furnace is purged with purified O_2 or 10% O_2 /Ar before the crucible is sealed. The temperature is ramped slowly at 2°C/min to 700°C to drive off any absorbed water, then quickly ramped (20°C/min) to reaction temperature. Hold times vary from 0.3 to 15 h.

2.4 Thin film characterization

X-ray diffraction data were collected with a Rigaku DMAX-A diffractometer using Ni-filtered Cu K_α radiation. Film thickness was measured by a Tencor P10 profilometer. Fluorine content was monitored by Hitachi 4500 SEM using Cambridge Scientific EDX analysis with light element window. Magnetic susceptibility measurements were made using a Quantum Design SQUID. T_c and J_c , on 80 μ m wide patterned bridges, were measured using the 4-point probe instrumentation described elsewhere.[8]

3. DISCUSSION

3.1 Precursor design

Any efficient MOCVD process relies critically on the availability of high purity metal-organic precursors with high, stable vapor pressures. An important approach to realizing such precursors is to minimize molecular oligimerization by saturating the metal coordination sphere with sterically hindered and/or fluorinated ligands. Of equal importance is that the precursor has suitable reactivity at deposition temperatures without prior gas phase decomposition. Until the discovery of HTS materials, the development of alkaline and rare earth metal MOCVD precursors had been largely neglected.

Generally, the four classes of volatile metal compounds are organometallic, halide, alkoxide, and coordination compounds (such as β -diketonates). Volatile organometallic compounds of alkaline and rare earth metals are known, however they tend to be extremely oxygen-sensitive, rendering transport in an oxidative environment difficult. Halide CVD has been utilized in HTS materials, however difficulties exist in transporting the relatively nonvolatile halides and in adjusting the thermodynamics to form oxides.[9] Alkoxides are utilized in the growth of oxide thin films (such as $BaTiO_3$ with $Ti(OCH_2CH_3)_4$).[10] However, many alkoxides tend to be oligomeric (especially with non-bulky ligands), have low vapor pressures, and are air sensitive. β -diketonates form complexes with most metals

A.

B.

Figure 2A. Ba(hfa)₂•mep, a stable liquid barium precursor used in this study for the growth of TBCCO thin films. B. Novel ketoiminate ligand forming a readily sublimable Ba complex.

and offer great versatility in chemical modification. One strategy for modification is to use the sterically encumbered *t*-butyl group in the dipivaloylmethanate (dpm, 1,1,6,6-tetramethylheptane-2,4-dione or tmhd) ligand. However, with electropositive metals having large ionic radii, the dpm ligand is not effective in reducing lattice oligomerization. Thus, dpm complexes of Ba, Sr and La have low volatilities. To achieve suitable vapor pressures these dpm compounds must be heated to near the respective decomposition temperatures, resulting in unstable vapor pressure characteristics and unreliable CVD processes. In particular, a stable precursor for

Ba would be highly desirable.

To reduce lattice cohesive energies, large bulky fluorinated ligands can be used. Bis(tetradecafluorononanedionato)aquobarium(II), Ba(tdfnd)₂•H₂O, had been employed for the growth of BaF₂ films at a source temperatures 40°C less than typically used for Ba(dpm)₂. [11] Another very attractive strategy is to use the electron withdrawing ability of fluorinated ligands to promote the coordination of neutral, electron-rich, ancillary ligands, thus further saturating the metal coordination sphere. Meinema, *et al.* employed a coordinated polyether around the Ba²⁺ ion in Ba(hfa)₂•tet. [12] They found that the compound sublimates as a monomer at temperatures 100° C less than Ba(dpm)₂. This technique has been similarly applied in the Ba(tdfnd)₂ system with the coordination of tetraglyme. [13] Of particular importance here is the low melting point of this compound. A liquid precursor eliminates vapor pressure instabilities that can arise from varying surface area of powders due to sintering effects. Another approach to lowering the precursor melting point is to modify the coordinating polyether. Using unsymmetric polyethers, Neumayer, *et al.* developed volatile Ba(hfa)₂•methylbutylhexaglyme with a melting point as low as 52°C. [14] The related Ba(hfa)₂•mep (mep = methylethylpentaglyme) (Figure 2A) has a melting point of 110°C and is used as a liquid Ba source in the present study of TBCCO growth.

A disadvantage of the fluorinated precursors is that at deposition temperatures of 350-780° C, fluorides are incorporated in the growing film from decomposing ligands. However, without the electron-withdrawing fluorinated ligands, polyethers do not form stable complexes. An alternative approach is to attach polyethers directly to the β-diketonate ligand to stabilize the coordination of the polyether. Work in this laboratory used polyethers attached to ketoiminate ligands and demonstrated useful volatility in this class of complexes for the growth of BaPbO₃ films by MOCVD. A related compound with the polyether spanning two β-ketoiminate ligands has also been recently synthesized (Figure 2B). The crystal structure shows the compound to be coordinately saturated. [16]

3.2 Reduced pressure thermogravimetric analysis

In order to have a controlled MOCVD process, the vapor pressures of the metal-organic precursors must be thoroughly characterized. However, many HTS metal-organic precursors have relatively low vapor pressures (< 0.2 Torr under usual deposition conditions) which makes vapor pressure measurement difficult. To study vapor pressures in the 10^{-9} to 10^{-4} Torr range, it is possible to use high vacuum evaporation rates combined with the Knudsen-Langmuir equation. For vapor pressures greater than 5 Torr, it is possible to use either transpiration methods or to measure the boiling point directly. To measure vapor pressures between 10^{-4} and 5 Torr, the pressure must be directly measured with a manometer using a rigorously sealed and evacuated chamber.[17] This method can encounter great experimental difficulties due to the formation of decomposition products and other volatile impurities. With great care, reliable data can be obtained.[18] However, data describing diffusion of MOCVD precursors cannot be acquired using this method. Under typical MOCVD conditions, total system pressures range from 1 to 20 Torr and non-equilibrium diffusion effects can be significant. A useful technique is to measure the evaporation rate of a precursor using thermogravimetric analysis (TGA) techniques under reduced pressure. From this dynamic procedure, information concerning operational vapor pressure and diffusion can be obtained.

The evaporation rate in high vacuum relates to equilibrium vapor pressure by the Knudsen-Langmuir equation,[19]

$$j = \alpha P_E (M/2\pi kT)^{1/2} \quad (1)$$

where j is the evaporation rate per unit area, α is the condensation coefficient, P_E is the equilibrium partial pressure, M is the molecular weight, k is the Boltzmann constant, and T is temperature. At higher pressures of inert gas, diffusion effects become important. The Langmuir equation becomes,

$$j = \frac{\alpha(P_E - P_x)(2\pi MkT)^{-1/2}}{1 + \alpha(x/D)(kT/2\pi M)^{1/2}} \quad (2)$$

where P_x is the pressure of the compound at distance x from the surface, and D is the diffusion coefficient. At the limit of high total pressures (small D), this becomes Fick's first law of diffusion.

There are several examples of reduced pressure TGA being used to study the volatility of MOCVD precursors. Takahashi, *et al.* used the classic Langmuir relation to describe the volatility of organic monomers for use in vapor deposition polymerization.[20] They note a sublimation rate decrease with increasing total pressure, which they attribute to a pressure dependent α term in eq.(1). At the lowest attained total pressure of 10^{-4} Torr, they assumed $\alpha = 1$ to calculate the equilibrium vapor pressures. However, the assumption of $\alpha = 1$ is not generally valid, and α can vary by several orders of magnitude for organic powders.[17] Strictly speaking, α is independent of inert gas pressure and cannot be measured for undefined powder surfaces without knowledge of equilibrium vapor pressure. The observed decrease in evaporation rate with total pressure is more likely diffusion-dependent, as described by eq.(2). Chou, *et al.*, measured the dynamic evaporation rates of $\text{Ba}(\text{dpm})_2$, $\text{Ca}(\text{dpm})_2$, $\text{Cu}(\text{dpm})_2$ at 20 Torr total pressure, which is near typical low pressure MOCVD conditions.[21] They reported a decrease in sublimation rate with time which they attributed to sintering and change in height of the precursors in the sample pans. Due to ambiguity in sample preparation in relation to sample height and area, diffusion data were not obtained, and the effects of sintering were not discerned. In this contribution we report a simple reduced pressure TGA experiment that allows measurement of the product of the diffusion

Figure 3. A: Effect of N_2 pressure on sublimation rate of Cu(dpm)_2 at $115^\circ\text{C}/5\text{ Torr}$ N_2 pressure as measured by reduced pressure TGA. Under typical MOCVD conditions, diffusion effects dominate precursor transport. B: Sublimation rate of Cu(dpm)_2 at $120^\circ\text{C}/5\text{ Torr}$ N_2 pressure as a function of diffusion distance x . Diffusion distance, x , is calculated from %weight times pan height. Inset shows Fick's law diffusion model to find $P_0 D$, with underlying solid line a fit to experimental data.

coefficient times the equilibrium vapor pressure of MOCVD precursors. This allows for a controlled comparison of precursor volatility in the MOCVD environment. With the equilibrium vapor pressure of the compound known, the diffusion coefficient can be calculated.

The rate of sublimation in a TGA experiment is calculated from the derivative of weight with respect to time divided by molecular weight and the area of the crucible. Figure 3A shows that for representative Cu(dpm)_2 , the rate of evaporation is significantly reduced as the ambient pressure is increased, which indicates that diffusion is a limiting factor in the transport of these precursors. With diffusion effects being important under these conditions, the distance that the precursor must travel from the surface of the powder to the top of the crucible is a significant factor. Figure 3B shows the evaporation rate as a function of distance from the solid precursor surface to the edge of the crucible ($x = \text{weight}/\text{full-weight} \times \text{crucible height}$). Over a distance of 3.4 mm, a 3-fold decrease in sublimation rate is seen at 5 Torr total pressure. The same reduction in evaporation rate is seen for liquid precursors of similar volatility, thus sintering over time is not the dominant cause of volatility reduction. To model the sublimation rate, note that the measured weight loss rate is the flux of precursor from the top of the pan into the carrier stream (j_x). We assume that this rate is proportional to the pressure of precursor at this plane on top of the pan (P_x) and to the diffusion coefficient (D) (eq.(3)),

$$j_x = KDP_x, \quad P_x = j_x / KD \quad (3)$$

where K is a constant dependent on the geometry of the crucible surface with respect to the carrier stream. At slow temperature ramp rates, steady-state conditions exist, and j_x is equal to the flux of precursor from the surface of the powder to the top of the pan. This flux is described by Fick's first law of diffusion (eq.(4)). Substituting P_x from (3) into (4) yields (5),

$$j_x = \frac{D}{x}(P_E - P_x) = \frac{D}{x}(P_E - \frac{j_x}{KD}) \quad (4)$$

Figure 4. Comparison of volatilities of six HTS MOCVD precursors determined by reduced pressure TGA. Conditions: 5 Torr total pressure; N_2 flowing at 100 sccm; temperature ramp rate of $1.5^\circ\text{C}/\text{min}$. Sublimation rates are normalized to a diffusion distance of 1.7 mm. Inflection points show melting points of the various precursors.

where P_E is the equilibrium vapor pressure of the precursor at the surface of the powder and x is the distance from the powder surface to the top of the pan. A two parameter curve fit of experimental j_x vs. x yields the product DP_E and K . Unfortunately, this single experiment cannot separate vapor pressure and diffusion effects. Since the equilibrium vapor pressure of $Ba(hfa)_2 \cdot tet$ is known from direct manometric measurements,[18] the resulting diffusion coefficient calculated from $P_E D$ is $1.5 \times 10^{-4} \text{ m}^2/\text{s}$ at 115°C , 5 Torr N_2 . Thus, it can be seen that a boundary layer of several millimeters from precursor surface to carrier stream can have dramatic effects on the evaporation rate. From these reduced pressure TGA experiments, it is readily apparent that diffusion plays a dominant role in the transport of the metal-organic precursors. This is of particular importance when designing transport evaporators for an MOCVD reactor. These effects can also be seen in the slopes of Arrhenius plots of the $\ln(\text{sublimation rate})$ vs. $1/T$ for $Ba(hfa)_2 \cdot tet$ which yield activation energies for the sublimation process. At total N_2 pressures of 6.0 Torr, the activation energy for $Ba(hfa)_2 \cdot tet$ vaporization is 1.70 kJ/mol; at 4.0 Torr, 1.50 kJ/mol; and at 0.1 Torr 1.23 kJ/mol. These data can be compared to the enthalpy of vaporization of 1.08 kJ/mol from the equilibrium vapor pressure data.[18] As the diffusion coefficient is generally described to be thermally activated, the activation energy for the sublimation process would be expected to be the sum of the vaporization enthalpy and diffusion activation energy terms. Since the sublimation rate is strongly dependent on diffusion, equilibrium vapor pressure data alone cannot be used to find the optimal temperature for a given transport rate. Typically, for precursor transport, the conditions of flow rate, pressure, and temperature must be empirically determined for a given evaporator geometry.

Figure 5. Vapor pressure temporal stability of important Ba MOCVD precursors at film growth temperatures. Sublimation rate is measured at 5 Torr N_2 . Between points, the TGA is backfilled with 1 atm N_2 , where the sublimation rate is negligible. The commonly used $Ba(dpm)_2$ temporal stability is poor compared to the fluorinated precursors.

Figure 6. Growth rate of $BaO(F)$ films as a function of carrier gas flow rate through the $Ba(hfa)_2 \cdot mep$ precursor reservoir. Conditions: 5 Torr total pressure; 350 sccm O_2/H_2O oxidizer; total flow 500 sccm with Ar dilution; 500° C substrate temperature. Cross hatches show the relative precursor weight loss at 25 and 150 sccm carrier flow. Inset shows gas phase stoichiometry during film growth as measured by precursor weight loss. $BaCaCuO$ film stoichiometry is measured by ICP atomic emission spectroscopy.

various precursors under MOCVD film growth conditions. At typical MOCVD pressures, diffusion effects are substantial and reactor design must reflect this. Fluorinated barium polyether adduct precursors are demonstrably more volatile and stable for MOCVD film growth.

3.3 Growth of $BaCaCuO(F)$ thin films

The MOCVD process is complex and can be described in the following steps: 1) volatilization of the precursor into the carrier stream, 2) transport of the precursor to the hot reaction zone, 3) surface absorption of the precursor and other reactive species, surface migration, and decomposition, 4) surface

Having characterized the diffusion effects in the TGA sample pan, the evaporation rate vs. temperature data can be normalized to a diffusion distance of 1.7 mm. The relative volatilities of some common HTS MOCVD precursors are shown in Figure 4. The fluorinated $Ba(hfa)_2 \cdot tet$ and $Ba(hfa)_2 \cdot mep$ sources are more volatile than $Ba(dpm)_2$ and sublime at temperatures far below the respective decomposition temperatures. This characteristic is critical for MOCVD process control since decomposing precursor will produce an unstable vapor pressure, and film stoichiometry will be uncontrollable. Also of importance is that $Ba(hfa)_2 \cdot mep$ is a liquid at deposition temperatures (which aids in growth reproducibility) and is 3 times more volatile than $Ba(hfa)_2 \cdot tet$ at 120°C.

To demonstrate the stability of $Ba(hfa)_2 \cdot mep$ and $Ba(hfa)_2 \cdot tet$ compared to $Ba(dpm)_2$, the evaporation rates were measured at various times over the course of four days at film growth temperatures. The TGA chamber was backfilled to atmospheric N_2 pressure between measurements to minimize weight loss (since the diffusion of the precursor at atmospheric pressure is negligible). As is readily apparent in Figure 5, the fluorinated alkaline earth precursors have much improved vapor pressure temporal stabilities whereas $Ba(dpm)_2$ decomposes substantially over the course of 20 hours.

In summary, reduced pressure TGA is a powerful tool to measure the volatilities of

migration and formation of the crystalline solid film, and 5) removal of the organic by-products. In many MOCVD processes, the second step is known to be rate-limiting, and reactor design considerations provide a constant supply of gaseous precursor over the area of the deposition zone. As described in the Experimental Section, the present MOCVD reactor design is employed to provide a uniform supply of precursor over a large substrate area. To determine whether the film growth rate is limited by mass transport effects, it is necessary to elucidate the relationship of precursor partial pressure to deposition rate. Figure 6 shows that as the carrier flow through the precursor reservoir is increased from 25 to 150 sccm (with constant total carrier flow) the deposition rate increases approximately linearly. Under conditions of constant total carrier flow rate, a doubling of the precursor flow rate should ideally double the concentration of precursor in the carrier stream and hence double the deposition rate. However an

Figure 7. MOCVD deposition rate vs. substrate temperature for BaCaCuO thin films using Ba(hfa)₂•mep, Ca(hfa)₂•tet, Cu(dpm)₂ precursors. Conditions: 5 Torr total pressure; 350 sccm oxidizer flow; 150 sccm total Ar carrier flow. A) With H₂O and O₂ oxidizing stream. B) Only O₂ oxidizer C) Only O₂ oxidizer and Cu(dpm)₂ precursor.

increase in deposition rate by only a factor of 1.5 is seen when the precursor stream flow rate is doubled. With a diffusion limited sublimation rate, the precursor carrier gas will not reach saturation and higher flow rates will dilute the pressure of precursor. Hence the deposition rate should not be directly proportional to precursor flow rate. At flows much higher than 150 sccm (the maximum for the present apparatus), deviation from the observed linear relationship would be expected. Also of importance are the crosshatched points in Figure 6 that show the relative precursor weight loss for precursors at the reservoir flow rates of 25 and 150 sccm. Both the deposition rate and precursor rate increase by a factor of 3.3. The deposition rate is directly proportional to precursor transport rate and hence to the precursor partial pressure in the total carrier stream, as expected for a mass transport-limited process.

As suggested by the TGA experiments, the diffusion of the precursor into the carrier stream is a limiting factor in the sublimation rate and it would thus be difficult to achieve equilibrium precursor pressures in the carrier stream. From the precursor weight loss and carrier gas volume, the ideal gas law partial pressure of Ca(hfa)₂•tet is estimated to be ~0.005 Torr in the carrier stream, while equilibrium vapor pressure is near 0.2 Torr.[18] Thus, the specifics of reservoir design in terms of diffusion distance are an important

factors for HTS MOCVD processes. If film growth is mass transport-limited, then the gas phase stoichiometry should be the same as that of the deposited film. The inset in Figure 6 shows that the gas phase stoichiometry as measured by precursor weight loss is identical to that of the deposited film as measured by ICP.

To further demonstrate the mass-transport limited character of BaCaCuO growth, deposition rate versus substrate temperature data are shown in Figure 7. The precursors used were Ba(hfa)₂•mep, Ca(hfa)₂•tet, and Cu(dpm)₂, and the oxidizer stream was O₂ and H₂O. It can be seen that a transport-limited growth regime begins at temperatures near 350°C. This is interesting because for the MOCVD of YBa₂Cu₃O₇ using non-fluorinated Y(dpm)₃, Ba(dpm)₂, Cu(dpm)₂ precursors, a mass transport-limited regime was found at temperatures greater than 600°C.[22] The decomposition of the hfa ligands is apparently more facile, which is surprising in view of the fact that fluorinated ligands produce more Lewis acidic metal centers which in turn form more stable adducts with the polyether glymes. Since the deposition rates here are similar to those observed in other studies (~20 nm/min)[22], the depression in the onset temperature for mass transport-limited kinetics is not due to a lower mass transport rate. In principle the effect of H₂O on the decomposition reaction could be great since it could act as a proton source to form volatile Hhfa byproducts. To explore this possibility, the above experiment was conducted without water in the oxidizing stream. The same general results were observed with mass transport-limited deposition beginning near 400°C (Figure 7B). The deposition characteristics of Cu(dpm)₂ under the conditions of Figure 7B are markedly different. At 400°C, there is essentially no Cu deposition. A possible explanation is that the decomposition products of Ba(hfa)₂•mep and Ca(hfa)₂•tet form Cu(hfa)₂ which is then etched from the film. There is precedent for Cu(hfa)₂ being formed in the selective etching of Pd/Cu surfaces.[23] The temperature vs. deposition rate plot for Cu(dpm)₂ in Figure 7C shows a rather constant growth profile that gradually increases with temperature. This is consistent with the results of Schmaderer, *et al.* [22] which reveal a very shallow increase in CuO deposition rate from 400°C-900°C. The diminution of CuO deposition at 400°C seen in Figure 7B requires the presence of fluorinated precursors and the absence of H₂O. Note that in the experiment shown in Figure 7C, metallic Cu deposits at lower temperatures from Cu(dpm)₂ alone.

To test the hypothesis that copper can be etched from BaCaCuO(F) films as Cu(hfa)₂, the volatile metal byproducts of Ba(hfa)₂•mep, Ca(hfa)₂•tet, Cu(dpm)₂ codeposition were trapped at 0°C shortly after passing the gaseous mixture through a resistively heated tube at 400°C. The trapped solids were then analyzed by mass spectrometry. When the products of the MOCVD reaction at 400°C without H₂O in the oxidizer stream (as in Figure 7B) were analyzed, both Cu(hfa)₂ and Cu(hfa)(dpm) were present under conditions where CuO etching was prevalent. However, when the products of the MOCVD reaction at

400°C with H₂O in the oxidizer stream (as in Figure 7A) were analyzed, Cu(hfa)₂ was also observed (without CuO etching). Thus, ligand exchange is operative without simultaneous etching of CuO. It is important to note that no Cu(hfa)₂ is seen when the carrier stream is condensed without

Table 1. Typical MOCVD growth conditions for BaCaCuO films having 2:1:2 cation stoichiometry

Precursor bath temperatures	116°, 86°, 112° C for Ba,Ca,Cu
Precursor carrier flow	50-100 sccm each
O ₂ /H ₂ O flow	100/250 sccm
Total pressure	5 Torr
Substrate temperature	500°C
Growth rate	1.2 µm/hr
Substrate	(110) single crystal LaAlO ₃

Figure 8. SEM micrograph of an MOCVD-derived Tl-2212 film showing characteristic platelet morphology.

diffraction. Due to the use of fluorine-containing metal-organic precursors, fluorides are readily incorporated into the film. To reduce the fluoride content, H_2O is used in the oxidizer stream to fluorides as volatile HF . To remove all fluorides *in-situ*, high deposition temperatures (780°C) are required. However, as described in the Tl-anneal section (see below), the fluoride content in the BCCO precursor film is not a critical factor, and deposition can be carried out at lower temperatures to enhance film morphology and to grow larger area films.

3.4 Formation and characterization of $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4+2n}$ thin films

The equilibrium pressure of Tl_2O over bulk Tl-2223 at phase formation temperatures is near 10 Torr.[24] This relatively high pressure combined with the extreme reactivity of Tl_2O renders an in-situ MOCVD process a daunting challenge. Therefore to form the TBCCO superconducting phases, the MOCVD-derived $\text{BaCaCuO}(\text{F})$ (BCCO) precursor films are annealed over bulk TBCCO pellets, thereby providing the equilibrium Tl_2O vapor pressure as in eq.(6). The subscripts of the reactant $\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_x(\text{film})$ refer to the cation stoichiometry ($n = 2,3$), of the BCCO film.

passing through the heated reaction zone.

From the study of deposition rate as a function of precursor transport and substrate temperature, it is found that the general mechanism of $\text{BaCaCuO}(\text{F})$ MOCVD growth is mass transport-limited with the present precursor system. H_2O in the oxidizer stream has little effect on film growth rate. Ligand exchange between precursors is observed and there is evidence for a CuO etching process.

Although the present MOCVD process is chemically complex, thin films of uniform composition over large areas can be readily grown. The conditions for the growth of $\text{BaCaCuO}(\text{F})$ films with 2:1:2 Ba:Ca:Cu cation stoichiometry are shown in Table 1. This simple reactor design affords a uniform deposition rate of 20nm/min ($\pm 5\%$ measured thickness in a 16 cm^2 area). Crystalline phases of CaO , Ba_2CuO , and BaF_2 are observed in the deposited thin films by x-ray

This Ti_2O pressure over the bulk pellet is strongly dependent on the annealing temperature and O_2 pressure as is seen by the equilibrium in eq.(7), with higher Ti_2O pressures achievable at lower O_2 pressures. The temperature required to form the Tl-2212 phase decreases markedly as O_2 pressure is decreased, with Tl-2212 phase forming at $820 \pm 5^\circ\text{C}$ and $895 \pm 5^\circ\text{C}$ for 10% and 100% O_2 , respectively. The Tl-poor Tl-1212 phase is commonly seen outside of this range of conditions. That the Ti_2O pressure control is key to TBCCO phase stability is strongly supported by the results of Aselage, *et al.*, in two-zone furnace experiments where Ti_2O pressure is controlled.[24] It is important to note that no fluorides are detected in annealed MOCVD films by windowless EDX, Auger analysis, or XRD. BCCO precursor films grown at 500°C contain negligible fluoride after the Tl-anneal. The fluoride is presumably removed during the anneal as TlF which is volatile and thermodynamically favored.[25]

To form the Tl-2223 phase, the BCCO precursor film is annealed over a 1:2:2:3 $\text{Ti}_2\text{O}_3\text{:BaO:CaO:Cu}$ pellet in 10% O_2 at 820°C for 12 h. Lower O_2 pressures help to stabilize the growth of the Tl-2223 phase[26] and long annealing times (12h) are required. Films are shiny to the eye, and the surface morphology is dominated by evidence of a melt during phase formation as shown in Figure 8. Large platelets of $20\mu\text{m}$ dimensions and $500\text{\AA}$ step heights, as measured by profilometry, are seen. A θ - 2θ x-ray diffraction scan (Figure 9A) shows an essentially phase-pure Tl-2223 sample.[27] Only the (00l) peaks are observed, indicating that the film is highly *c*-axis oriented. The θ -rocking curve (a further measure of *c*-axis orientation) exhibits a full width at half maximum of 0.8° (Figure 9B) which is comparable to values for typical PVD-derived films. An in-plane ϕ -scan (Figure 9C) shows the relative orientation of the cell axes within the *c*-plane. Reflections appear every 90° as expected for an epitaxial.

Figure 9. (A) θ - 2θ x-ray diffraction pattern of an MOCVD-derived Tl-2223 thin film grown on (110) LaAlO_3 . (B) θ -rocking curve of the (0014) reflection of an MOCVD-derived Tl-2223 thin film grown on (110) LaAlO_3 . (C) ϕ -scan of the (109) reflection of an MOCVD-derived Tl-2223 thin film grown on (110) LaAlO_3 .

tetragonal TBCCO film.

Transport measurements provide further indications of film properties. The resistivity vs. temperature behavior of an MOCVD-derived Tl-2223 film (Figure 10A) indicates $T_c = 115$ K. Several films were patterned using standard photolithography and EDTA etching to define an 80 μm wide microbridge structure. Critical current density results from dc and pulsed transport measurements appear in Figure 10B. At 77 K, the highest $J_c = 1.5 \times 10^5$ A/cm², as defined by a 10 $\mu\text{V}/\text{cm}$ offset criterion. Bean model calculations using SQUID susceptometer data yield $J_c = 4 \times 10^6$ A/cm² at 5 K (0 T) and 6×10^5 A/cm² at 77 K (0 T). The 77 K J_c values obtained from the transport and magnetic measurements agree reasonably well, suggesting that intragrain coupling does not adversely affect the transport capacity of these films. These transport properties are comparable to those of the highest quality PVD-derived films. Figure 10C shows surface resistance measurements on a film containing some admixed Tl-2212 phase, performed in a parallel plate resonator against YBCO. This measurement yields $R_s = 0.35$ m Ω at 5 K, 10 GHz, approaching the lowest values reported for PVD-derived films. MOCVD-derived Tl-2212 thin films are also of high quality with $T_c = 105$ K, and $R_s = 0.4$ m Ω (5 K, 10 GHz).

3.5 Growth of dielectric oxide thin films

Many advanced HTS devices require low dielectric loss, lattice-matched thin films for buffer layers or for insulating layers in superconductor/insulator/superconductor (SIS) structures. Efficient MOCVD growth processes for these dielectric materials must be developed along with those for HTS materials. MOCVD has been implemented in the growth of oxide systems such as MgO[28], YSZ[29], and CeO₂[30].

Figure 10. A. Variable temperature resistivity vs. temperature data for an MOCVD-derived Tl-2223 thin film grown on (110) LaAlO₃. B. Critical current vs. temperature for an MOCVD-derived Tl-2223 thin film grown on (110) LaAlO₃. C. Temperature vs. surface resistance of an admixed phase Tl-2223/2212 film. The dashed line is a plot of the London Model with offset included.

Figure 11A. $\theta/2\theta$ XRD scan showing MOCVD derived (001) oriented SrPrGaO₄ film grown on LaAlO₃. B. θ -rocking curve showing FWHM of 0.46° for the (002) reflection. C. ϕ -scan showing in-plane epitaxy with the 4-fold symmetry of tetragonal SrPrGaO₄.

however materials with smaller HTS lattice mismatches (<1%) and greater chemical inertness are of great interest.

Recent efforts in this laboratory achieved the *in-situ* epitaxial growth of YAlO₃ films on LaAlO₃ substrates using Y(dpm)₃ and Al(acac)₃ as precursors.[31] A substrate temperature of 800°C and N₂O oxidizer gas were used. Epitaxy is seen in the four-fold symmetry of the ϕ -scan, and sharp interfaces are apparent in cross-sectional high resolution TEM. However, domains of (110) and (001) film growth are also seen by TEM (the reflections overlap in XRD experiments). The source of the (110) and (001) domains is the close similarity in orthorhombic lattice parameters. To circumvent this, the growth of cubic dielectrics has been investigated. Thus, Sr₂AlTaO₆ films have been grown *in-situ* using Sr(hfa)₂•tet, Al(acac)₃, and [Ta(OEt)₅]₂ precursors with a substrate temperature of 850°C and N₂O as the oxidizer.[32] Films are epitaxial by XRD analysis, and high resolution TEM shows no domain boundaries. Also of great interest is tetragonal LaSrGaO₄ which, along with a close YBCO lattice and thermal expansion coefficient match, has no phase transitions from low temperature to 1520°C, thus eliminating twinning.[33] Recently in this laboratory, thin films of the closely related compound, SrPrGaO₄, have been grown for the first time on LaAlO₃ by MOCVD using Sr(hfa)₂•tet, Pr(dpm)₃, and Ga(dpm)₃ precursors with N₂O as the oxidizer at 810°C.[34] The XRD data shown in Figure 11A indicate phase pure *c*-axis oriented SrPrGaO₄ on LaAlO₃. The sharp rocking curve and 4-fold symmetry

of the in-plane scan demonstrate epitaxy (Figures 11B-C).

Orthorhombic PrGaO₃ films have also been grown on LaAlO₃ by MOCVD using Pr(dpm)₃ and Ga(dpm)₃ at temperatures of 750-850°C with N₂O as the oxidizer. Films are epitaxial by XRD, but the subtle (110) and (001) growth domains are again seen in TEM. However, both domains have nearly identical lattice spacings which are well-matched to YBCO (0.1%). Onto this buffered substrate, epitaxial YBa₂Cu₃O_{7-x} films have grown by both pulsed laser deposition (PLD) and pulsed organometallic beam epitaxy (POMBE). Figures 12A-C shows XRD data demonstrating epitaxial growth of YBCO by PLD on the MOCVD-derived epitaxial PrGaO₃ dielectric layer. The superconducting properties are excellent with $T_c = 91\text{K}$ and $J_c(77\text{K}) = 6 \times 10^6 \text{ A/cm}^2$. [35] This

Figure 12A. $\theta/2\theta$ XRD scan showing a YBCO/PrGaO₃/LaAlO₃ multilayer structure. B. ω -rocking curve showing FWHM of 0.49° for (005) reflection of YBCO indicating high quality. C. ϕ -scan showing in-plane epitaxy with the substrate for both YBCO and PrGaO₃.

demonstrates that MOCVD can be effectively used in the growth of important dielectric/substrate films for HTS applications.

4. CONCLUSIONS

There has been significant progress in the development of MOCVD for HTS applications. Through careful ligand design, volatile, thermally stable Ca, Sr, and Ba precursors are now available. In particular, designed polyether adducts of fluorinated Ba complexes are liquids under film growth conditions and thus exhibit stable vapor pressure characteristics. For example, the liquid source, Ba(hfa)₂•mep, has been implemented in the successful growth of TBCCO superconductor thin films. In the development of fluorine-free Ba sources, a novel complex has also been developed in which the polyether lariat is connected to β -ketoiminate frameworks. In understanding the volatilization of HTS MOCVD precursors, a novel thermogravimetric analysis method has been developed. Information about both vapor pressure and vapor diffusion are obtained, and diffusion effects are shown to be significant under typical MOCVD film growth conditions. BaCaCuO films are readily grown by MOCVD. The process is mass transfer-limited at low temperatures (near 350°C), and interesting ligand exchange processes are detected. High quality Tl-2223 and 2212 films are formed from BaCaCuO(F) films annealed in the presence of Tl₂O diffusing from bulk TBCCO pellets at 820-895°C. Film transport properties are comparable to those of the best PVD-derived films with T_c values as high as 115K and surface resistances as low as $0.35\text{m}\Omega$ at 5K (10GHz).

MOCVD routes to dielectric oxide films have also been realized with epitaxial YAlO₃, Sr₂AlTaO₆, SrPrGaO₄, and PrGaO₃ growth demonstrated on LaAlO₃. A multilayer structure has been fabricated with high quality epitaxial YBCO grown upon MOCVD-derived PrGaO₃. In summary MOCVD has been successfully used to grow high quality superconducting thin films and dielectric layers which are applicable to the fabrication of HTS-based devices.

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