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Aspects of the SrO-CuO-TiO_2 Ternary System
Related to the Deposition of SrTiO_3 and
Copper-Doped SrTiO_3 Thin-Film Buffer Layers

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Aspects of the SrO-CuO-TiO₂ Ternary System Related to the Deposition of
SrTiO₃ and Copper Doped SrTiO₃ Thin Film Buffer Layers

Dear Ms. Ayala:

Congratulations! I am pleased to inform you that your dissertation has received all necessary approvals and has been accepted in partial fulfillment of the requirements for the doctoral degree.

On behalf of the University, I send you our very best wishes for your continued success.

Sincerely,

Teresita E. Aguilar, Ph.D.
Dean, Graduate Studies

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**ASPECTS OF THE SrO-CuO-TiO₂ TERNARY SYSTEM
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COPPER DOPED SrTiO₃ THIN FILM BUFFER LAYERS**

by

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Submitted in Partial Fulfillment of the
Requirements for the Degree of

**Doctor of Philosophy
Engineering**

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December 2004

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by

Alicia Ayala

Dedicatoria

Para mi papá, mi mamá, y mi hermana

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Alicia Ayala

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ALICIA AYALA

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ABSTRACT

$\text{YBa}_2\text{Cu}_3\text{O}_{7-8}$ (YBCO) coated conductors are promising materials for large-scale superconductivity applications. One version of a YBCO coated conductor is based on ion beam assisted deposition (IBAD) of magnesium oxide (MgO) onto polycrystalline metal substrates. SrTiO_3 (STO) is often deposited by physical vapor deposition (PVD) methods as a buffer layer between the YBCO and IBAD MgO due to its chemical stability and lattice mismatch of only $\sim 1.5\%$ with YBCO.

In this work, some aspects of the stability of STO with respect to copper (Cu) and chemical solution deposition of STO on IBAD MgO templates were examined. Solubility limits of Cu in STO were established by processing Cu-doped STO powders by conventional bulk preparation techniques. The maximum solubility of Cu in STO was $\sim 1\%$ as determined by transmission electron microscopy (TEM) and Rietveld refinements of x-ray diffraction (XRD) data. XRD analysis, performed in collaboration with NIST, on powder compositions on the STO/SrCuO_2 tie line did not identify any ternary phases.

$\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ buffer layers were prepared by pulsed laser deposition (PLD) and CSD on IBAD MgO flexible metallic textured tapes. TEM analysis of a ~ 100 nm thick $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$

buffer layer deposited by PLD showed a smooth Cu-doped STO/MgO interface. A ~600 nm thick YBCO film, deposited onto the $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ buffer by PLD, exhibited a T_c of 87 K and critical current density (J_c) of ~1 MA/cm². STO and Cu-doped STO thin films by CSD were ~30 nm thick. The in plane alignment (FWHM) after deposition of the STO improved by ~1° while it degraded by ~2° with the $\text{SrCu}_{0.05}\text{TiO}_y$ buffer. YBCO was deposited by PLD on the STO and $\text{SrCu}_{0.05}\text{TiO}_y$ buffers. The in plane alignment (FWHM) of the YBCO with the STO buffer layer slightly improved while that of the YBCO with the $\text{SrCu}_{0.05}\text{TiO}_y$ buffer layer remained constant. A goal of the CSD approach to fabrication of coated conductors is process simplicity. In this study, single layer textured films were obtained without a nucleating seed layer that has been deemed necessary by several investigators. These results indicate that Cu-doped STO buffer layers deposited by PLD or CSD are compatible with IBAD MgO and YBCO and that CSD is a viable approach to coated conductor fabrication.

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INTRODUCTION

To fly we have to have resistance.

— Maya Ying Lin (1959–____)
US architect, sculptor. She designed
the Vietnam War Memorial, dedicated 1982.

- 1.1 SUPERCONDUCTIVITY
- 1.2 $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ SUPERCONDUCTORS
- 1.3 SOLUBILITY OF Cu IN SrTiO_3
- 1.4 $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ COATED CONDUCTOR FABRICATION
- 1.5 STATEMENT OF THE PROBLEM
 - 1.5.1 Scientific Problems and Objectives
 - 1.5.2 Engineering Problems and Objectives
- 1.6 REFERENCES

1.1 SUPERCONDUCTIVITY

The merging of superconductivity with electric power applications has been speculated upon since the phenomenon of zero resistivity was discovered in 1911 (1) in attempts to eliminate resistance losses in the energy flowing through a material. For example, electrical resistance results in a 10.6% loss of efficiency in current electrical transmission lines (2). Experiments conducted by Kamerlingh Onnes showed that zero resistance to the transport of electricity could be attained by cooling mercury metal to the boiling point of liquid helium (4.22 K) (1). Onnes coined the term “superconductivity” due to the unique quality exhibited by the material. Therefore, a superconductor is an element, inter-metallic alloy, or compound that will conduct electricity without resistance below a certain temperature, known as the superconducting critical temperature (T_c). Another characteristic property of superconductors is perfect diamagnetism, meaning that when cooled below the T_c in the presence of a magnetic field, a superconductor repels magnetic flux. In 1933, Walter Meissner and Robert Ochsenfeld recognized this phenomenon as the Meissner effect (3).

The occurrence of superconductivity is explained by the BCS theory (Bardeen, Cooper, and Schrieffer) in the weak coupling limit (3). The foundation of the BCS theory relies on an earlier discovery that showed that the ground state of a material is unstable with respect to pairs of bound electrons. The pairs of bound electrons, known as Cooper pairs, are the result of electron-phonon interactions in a lattice. Thermal vibrations of ions within the material lattice oscillate about their equilibrium positions leading to lattice vibrations, or phonons. As electrons move through the lattice, they interact with ions causing charge distortions that propagate along the lattice structure. The electron distorts the lattice around it creating an area of greater positive charge density around itself and in turn, attracting another electron at some distance in the lattice. The two electrons form a Cooper pair or a bound state of two electrons. Cooper pairs are responsible for carrying the supercurrent in a superconductor. The stability of the Cooper pair is greater than that of a single electron in the lattice, therefore its mobility through the lattice is more resistant to thermal vibrations. As temperature increases, the ability of Cooper pairs to overcome thermal vibrations is impaired, i.e., attainment of the weak coupling limit. Increased thermal energy results in greater electron-phonon interactions that impede the flow of electrons through the lattice. This phenomenon is observed in superconductors as superconductivity decreases with temperature or increasing magnetic field to the point of destruction.

Superconducting materials can be classified as either Type I or Type II superconductors (3). Type I superconductors or “weak coupled” superconductors require the coldest temperatures to become superconducting. They are characterized by a sharp transition to a superconducting state and exhibit complete repulsion of applied magnetic fields, a characteristic known as perfect diamagnetism. Diamagnetic materials have a negative response to an applied magnetic field or a negative magnetic susceptibility (χ), corresponding to a weakening effect on the surrounding magnetic field. Figure 1.1 shows the magnetic susceptibility behavior at the superconducting transition temperature. Type II superconductors or “hard” superconductors

Figure 1.1 Graph of temperature vs. resistance for a Type I superconducting material with corresponding temperature vs. magnetic susceptibility (χ) plot. Magnetic susceptibility is the degree of magnetization of a material in response to a magnetic field. Perfect diamagnets such as superconducting materials have a negative magnetic susceptibility because they weaken the surrounding magnetic field.

consist of metallic compounds, alloys, and oxides. They differ from Type I in that their transition from a normal to a superconducting state is gradual across a region of “mixed state” behavior. Type II superconductors are not characterized by perfect diamagnetism. Regardless of being Type I or Type II, once set in motion, electrical current will flow forever in a closed loop of superconducting material.

1.2 $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ SUPERCONDUCTORS

A milestone year for superconductivity was 1986 when IBM research scientists Bednorz and Muller announced the discovery of a Type II ceramic that became superconducting at 30 K (4). In 1987, Wu et al., published results indicating superconductivity in a Y-Ba-Cu-O (YBCO) compound at temperatures above 90 K (5). This led to an explosion of research on the YBCO compound. YBCO must be grown in ways that permit strong alignment of two orthogonal axes of the individual grains, referred to as biaxial texture, to allow for superconducting currents to flow across grain boundaries without loss (6). Techniques first developed by Iijima et al., using IBAD methods made the required biaxial texture possible and in doing so introduced YBCO coated conductors (7). Coated conductors have a tape-like geometry consisting of a series of layers. Figure 1.2 (a) shows a comparison of the respective geometries of coated conductors to the conventional copper (Cu) wires used in the current transmission grid (8). Figure 1.3 (b) shows a section of a 1 meter cable consisting of solution deposited YBCO coated conductor manufactured by American Superconductor. Figure 1.3 provides a TEM cross-sectional view of a YBCO coated conductor fabricated at Los Alamos National Laboratory. This particular coated conductor consists of 6 layers deposited onto a nickel alloy substrate.

Coated conductors consist of four parts (which do not limit the architecture to 4 layers): a textured template, intervening buffer layer(s), the superconducting film, and a passivating layer. The passivating layer is a metal such as Cu or silver (Ag). The steps involved in a manufacturing process are: textured substrate material preparation, buffer layer preparation and application, preparation and application of the high temperature superconducting (HTS) material and required post-annealing, and preparation and application of the passivating layer. In general, coated conductors are fabricated by depositing a superconducting material onto a long, flexible base material. A critical requirement of the base material is that it must be textured in a preferred orientation in order to promote biaxial growth (growth in one specified

Figure 1.2 Pictorial comparison of conventional copper wires used to transmit electricity in the current electric power grid. Approximately 10.6% of the electricity transmitted through copper wires is lost in the distribution process. In contrast, coated conductors, shown wrapped around the cu wires in (a), transmit electricity without any losses due to resistance (8). (b) In August 2003, American Superconductor manufactured a 1 meter cable by solution deposition that had a measured critical current density (J_c) of 4 MA/cm² (47).

Figure 1.3 TEM cross-sectional view of a YBCO coated conductor fabricated at Los Alamos National Laboratory. This particular coated conductor consists of six intervening layers between the nickel alloy substrate and the YBCO superconducting film. The buffer layer is YSZ. The passivating layer is not shown in this image.

orientation) of the buffer layers and superconducting film. Figure 1.4 shows a schematic diagram of a randomly oriented thin film and a biaxially textured film. A strongly oriented perpendicular texture with no preferred azimuthal orientation in the plane of the substrate is called a fiber texture. In addition to a strong perpendicular texture, it is often desirable to obtain an in-plane azimuthal texture. This combination is referred to as biaxial texture, and can range from a slightly asymmetric fiber texture to almost a single crystal orientation.

YBCO is most commonly used in coated conductors. Two competing buffer layers for the YBCO superconductor are yttria-stabilized zirconia (YSZ) and magnesium oxide (MgO). IBAD YSZ requires ~ 500 - 1000 nm of material to achieve an acceptable orientation of $\sim 12^\circ$ which translates to a deposition time of ~ 20 hours per meter (9). An ion beam assisted deposition (IBAD) MgO buffer layer can achieve comparable orientation with a thickness of only ~ 10 nm or a deposition time ~ 100 times faster when compared to that of IBAD YSZ (10). The drawbacks of combining YBCO and MgO are that the full extent of material interactions is not understood and required phase diagram information is not documented. These drawbacks are the subject of the current work.

Figure 1.4 Schematic diagram showing texture in a thin film. (a) Randomly oriented polycrystalline film. (b) Biaxially textured film. Biaxially textured films have a preferred out-of-plane orientation (side view) and a preferred in-plane orientation (top view).

1.3 SOLUBILITY OF Cu In SrTiO_3

Research has shown that optimum superconducting properties can be obtained through the use of two buffer layers (11). The function of the first buffer layer is two fold: to provide the biaxially textured template required for oriented growth of subsequent layers (11) and to prevent diffusion between the metallic substrate and the YBCO film (12). The second buffer layer improves the lattice mismatch between the YBCO (13) and the first buffer layer while diminishing the reactivity of the YBCO (14). The lattice mismatch between MgO and YBCO is 9.67% while that between STO and YBCO is only 1.5% (15). It is apparent that incorporating STO into the coated conductor architecture is beneficial for the alignment of the YBCO.

One of the speculated interactions between YBCO and MgO is that Cu from YBCO can diffuse into the MgO structure through direct interfacial contact or through neighboring layers. Parathaman et al., have shown that MgO can accommodate from 9 to 21 atomic percent Cu into its structure in a temperature range of 850°C to 1050°C (16). Figure 1.5 shows a compositional profile of a Cu depleted YBCO coated conductor. It is speculated that depletion of Cu from YBCO may compromise the superconducting properties. An intervening buffer layer for the YBCO/MgO combination is Cu-substituted SrTiO_3 . An approach to minimize material interactions involves the addition of excess Cu to the buffer layer adjacent to the YBCO with the intention of alleviating the Cu depletion resulting from the diffusion of Cu out of the YBCO and into the neighboring MgO (17). High-quality YBCO films are routinely grown on single-crystal STO substrates; however, the reactivity between YBCO and STO is undocumented. While interfacial reactions are absent during deposition onto single crystal substrates, the deposition of YBCO onto a textured, polycrystalline film of Cu-substituted STO may present a different story. YBCO and Cu-substituted STO exhibit compatibility in terms of lattice mismatch and chemical stability. YBCO has an orthorhombic structure with $a=0.382$ nm, $b=0.389$ nm, $c=1.168$ nm, whereas STO has a cubic perovskite structure with

Figure 1.5 Compositional profile of a YBCO coated conductor showing the diffusion of Cu from the YBCO through the buffer layers. This Cu out-diffusion from the YBCO layer may leave the YBCO Cu-poor and alter the critical temperature (T_c). The x-ray profile shows the presence of Cu in the Ni alloy substrate (47).

$a=0.3905$ nm. A schematic of the YBCO unit cell (18) is shown in Figure 1.6 and the STO unit cell (19) is depicted in Figure 1.7. The lattice mismatch across the interface is 0.38% along the YBCO [001] direction and 2.18% along the perpendicular direction, that is the [010] direction of TiO_2 . The mismatch between the STO surface plane and the YBCO oriented to c-axis is low which is conducive to the creation of epitaxial single crystal thin films. Preliminary studies on YBCO/Cu-substituted STO thin films indicate minimal interfacial reactions that affect YBCO alignment along the interface (20). This research tests the effectiveness of a Cu-doped STO buffer layer in improving lattice mismatch.

In order to identify optimum Cu-substituted STO thin film compositions, phase information for the SrO-CuO-TiO_2 system was researched. A phase diagram for the

Figure 1.6 Schematic of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ unit cell. The $\text{YBa}_2\text{Cu}_3\text{O}_7$ unit cell is a perovskite type cell with a 1:2 repeat stacking pattern of ABBABB... The unit cell has one yttrium atom located in the center of the unit cell (pink atom). Two barium atoms occupy the sites above and below the yttria atom (yellow). Copper atoms are denoted in maroon and oxygen atoms are denoted in red. $\text{YBa}_2\text{Cu}_3\text{O}_7$ can also exist as an oxygen deficient perovskite. This is expressed as $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. (18)

SrO-CuO-TiO_2 system was not found in the published literature. Binary phase diagrams are available for the SrO-CuO (21, 22), SrO-TiO_2 (23, 24), and CuO-TiO_2 (25) systems but a ternary combination of these has not been studied (Figure 1.8). One objective of this research became to determine a portion of the SrO-CuO-TiO_2 system that was vital to the study, in particular the STO/SrCuO_2 tie line. Initial compositions ranged from $x=0$ to $x=1$ for Cu and Ti in $\text{Sr}_1\text{Cu}_x\text{Ti}_{1-x}\text{O}_y$. Early solubility studies from this research showed that the STO crystal structure can accommodate low levels of Cu (20).

A significant issue encountered in the entire multi-layer arrangement is material compatibility along the various interfaces. The reactivity of the YBCO with the neighboring buffer layer needs to be addressed. The reaction of YBCO with various buffer layers has been investigated (26, 27). Studies have documented successful deposition of YBCO on STO single

Figure 1.7 Schematic of the STO unit cell. The STO unit cell is a primitive cubic perovskite type cell with a characteristic 1:1 repeat stacking pattern of ABABAB... The unit cell has one strontium atom located in the center of the unit cell (green atom). Titanium atoms occupy the corner sites (gray atoms). Oxygen atoms occupy the face centered sites (red atoms). (19)

crystal substrates (28-33) as well as on STO buffer layers (34-39). Microstructural analysis of the YBCO/STO interfacial region indicates the presence of one or more secondary phases along the interface (28-30) as well as diffusion of Sr and Ti into the YBCO layer (31, 32) and intermixing (33). However, the combination of MgO and CuO yields secondary phases. Possible secondary phases include Cu_2MgO_3 and a Cu substituted MgO rich solid solution (Cu^{2+} and Cu^+ ions can be accommodated by the MgO) (40). The formation of secondary phases can be detrimental to the performance of the multilayer superconductor. Research conducted by Foltyn et al., have shown that a YBCO layer thickness of 1-2 μm is optimum for maximum critical current (I_c) carrying capacity (41). Additional YBCO thickness beyond

Figure 1.8 Schematic of the SrO-CuO-TiO₂ ternary phase diagram investigated in this research and current binary phase diagrams for SrO-CuO (21, 22), SrO-TiO₂ (23, 24), and CuO-TiO₂ (25).

the 1-2 μm range hinders the current carrying capacity of the coated conductor due to the formation of reaction products or microporosity. A thicker film of YBCO requires longer deposition times at high temperature, thus providing ample opportunity for diffusion from the substrate to the YBCO. The result is a dead layer of secondary phases along the interface that reduces the cross section for current transport.

1.4 YBCO COATED CONDUCTOR FABRICATION

YBCO coated conductor production processes are the focus of technology assessments to develop a roadmap of the market directions of YBCO conductors and the improvements that are needed to ensure market acceptance. The recurring theme of these investigations is the high cost of deposition methods such as IBAD and pulsed laser deposition (PLD). Another important factor that must be considered in the processing of long coated conductors is the rate of production. Optimization of the YBCO deposition process must take into account the area that will be covered at a specified deposition rate. At the current rate of a few square centimeters per hour that can be achieved in the laboratory setting by PLD, the YBCO deposition operation is not scalable for industrial production that requires a minimum rate of a few square meters per hour (42). Film deposition rates must increase by four orders of magnitude to achieve economical manufacturing of long lengths of coated conductors.

Chemical solution (CSD) methods for thin film deposition have an advantage over other deposition techniques because they are capable of producing transparent, crack-free, polycrystalline thin films that are pure, homogeneous, and stoichiometric with relative ease (43). The required equipment is operational at atmospheric conditions, which translates into less complicated and less expensive start up (42). Development of the CSD technique for thin film deposition can be achieved in the research setting by spin coating, which involves small substrates, i.e., 1 cm $\times$ 1 cm substrates. This process is adaptable for large-scale production by applying similar basic deposition principles to the method of dip coating.

Broad scale commercialization of YBCO superconductors is hindered by the associated production costs of *in situ* deposition methods, such as PLD and IBAD that are used to prepare the various layers of coated conductors (44, 45). The cost of these methods keeps the price performance of the YBCO superconductor above the \$10 kA m⁻¹ limit, which is the current threshold for replacement of Cu on the electric utility grid (44-46). CSD is an alternate means of thin film fabrication at a lower cost when compared to *in situ* methods requiring vacuums and lasers. CSD can be used to introduce the Cu-substituted STO buffer layer into the coated conductor structure. Much research is needed on solution based deposition of STO and various materials of interest. Such a method must yield superconductors on par with those produced *in situ*. Application of STO solubility limits to the investigation of CSD fabrication techniques will provide further understanding of a key technology that can lead to economical YBCO superconductors.

1.5 STATEMENT OF THE PROBLEM

The scientific objectives of this research were to study a portion of the STO/SrCuO₂ tie line in the SrO-CuO-TiO₂ ternary system to establish solubility limits of Cu in STO, investigate the possibility of ternary phases, and examine the behavior of Cu-doped STO buffer layers for YBCO coated conductor applications. Understanding of the phase behavior was applied to the fabrication of a YBCO coated conductor with STO and Cu-doped STO buffer layers deposited by PLD and CSD for comparison of the fabrication methods. The buffer layer was deposited onto IBAD MgO templates.

This research was motivated by a possible compatibility issue of MgO/YBCO coated conductors which could lead to the migration of Cu away from YBCO into the MgO phase which accommodates up to 9 atomic percent Cu at 850°C and up to 21 atomic percent Cu at 1050°C into its structure (16). The diffusion of Cu away from the YBCO layer can depress the T_c. Cu migration can be addressed by introducing a Cu-doped STO buffer layer, saturated with Cu, adjacent to the YBCO layer to minimize Cu diffusion through the structure thus

maintaining YBCO stoichiometry. The additional Cu in the Cu-doped STO may also lead to the phenomenon of liquid phase sintering within the resulting microstructure. Liquid phase sintering refers to a sintering process involving a liquid and solid that coexist at a particular temperature (48). The combination of solid and liquid phases at the same temperature allows the liquid phase to disperse throughout the solid phase and bind the liquid and solid phases into one. Liquid phase sintering helps to reduce microstructural porosity. Preliminary studies have revealed the formation of a low melting temperature phase that serves the purpose of binding the microstructure and reducing inherent porosity to yield a denser structure (49, 50). It is speculated that densification of the microstructure will further limit Cu migration.

The STO and Cu-doped STO buffer layers were deposited by PLD and CSD. Bulk powder studies of the STO-SrCuO₂ system were done to provide fundamental understanding of phase behavior and solubility limits within the material system. Determination of the solubility limits of Cu in STO was important to assess the practicality of doping the STO buffer layer with the purpose of optimizing superconducting properties in the YBCO coated conductor.

1.5.1 Scientific Problems and Objectives

The lack of availability of phase diagram information for the SrO-CuO-TiO₂ system establishing solubility ranges limits the application of Cu addition to STO. The phase evolution of the system dictates the likelihood of adding Cu to STO to mitigate Cu diffusion away from the YBCO superconducting layer and into neighboring buffer layers. If the STO structure can accommodate Cu, the potential effects of the compositional modification merit investigation. Knowledge of the Cu solubility limits is essential, but only addresses a portion of the problem. The remaining question is whether or not the YBCO will react with the Cu-doped STO buffer layer. Information of the reactivity between YBCO and STO is limited and this extends to the STO with added Cu. Documentation of the reactivity of

YBCO and Cu-doped STO aids in the development of a pattern of microstructural evolution of Cu-doped STO thin films deposited by PLD and CSD techniques.

Solubility limits of Cu in bulk STO. A limitation encountered by this research was the lack of phase characterization for the material system of interest. Without such information, an in depth study of the system cannot be completed. Phase diagrams provide data that aids in the determination of appropriate operating temperatures in a range of compositions. It is critical to know how a material will behave at a certain temperature. Knowing the phase assemblage at a specific temperature and composition allows for control of properties in the material of interest.

Solubility limits of Cu in STO have not been previously documented. Emphasis in this work was placed on the microstructural evolution in the 0% to 20% Cu range of the STO/SrCuO₂ tie line, because according to preliminary studies, the solubility limit of Cu in STO is much less than 20% (49, 50). In order to develop a buffer layer that is compatible with the YBCO coated conductor in terms of minimizing or eliminating Cu migration away from the YBCO, knowledge of solubility of Cu in STO is essential. It has been shown that in the case of MgO buffer layers, the MgO can accept up to 9 atomic percent at 850°C and 21 atomic percent Cu at 1050°C into its structure (16). This can be detrimental to the superconductor performance. The Cu diffusion is perhaps triggered by extended exposure to temperatures during the post deposition conversion process. Part of this goal was to develop a Cu-doped STO buffer layer by implementing the solubility limits to determine a buffer layer composition that is compatible with YBCO to minimize Cu migration through the sequence of layers of the coated conductor.

Deposition of STO and Cu-doped STO thin films. The solubility limits provide some direction in terms of choosing optimum compositions for a Cu-doped STO buffer layer that is compatible with YBCO to the extent of minimizing Cu migration. PLD and CSD are two competing techniques for the deposition of buffer layers in coated conductors. The growth mechanisms of the two methods are dependent on the deposition source, a bulk powder target

for PLD and a liquid precursor solution for CSD. Identification of buffer layer compositions addresses only one step of the deposition process. The growth behavior of films deposited from bulk powders and liquid precursors was studied and compared.

1.5.2 Engineering Problems and Objectives

The engineering problems associated with STO and Cu-doped STO buffer layers in the YBCO coated conductor structure include the need for a buffer layer compatible with YBCO and the cost of production associated with physical deposition methods such as PLD and IBAD. IBAD is an accepted technique for the deposition of MgO onto the textured substrate. However, it is a slow process and scale up is complicated and expensive. Production costs can be minimized by combining IBAD with other less expensive deposition processes for buffer layers and YBCO such as CSD. While the deposition of the first buffer layer by IBAD has been optimized by selecting MgO over other buffer materials (6), economical deposition of YBCO by PLD requires a 4-fold increase of current deposition rates (7). The rate of deposition is an important parameter to consider but it must also be coupled with the area involved in the deposition. Laboratory PLD set ups can only achieve deposition of a few square centimeters per hour. Wide-spread use of coated conductors depends on scale-up capabilities of simple and economical processing methods. CSD methods offer a viable alternative.

Solubility limits. The established solubility limits were used to identify a composition for the Cu-doped STO buffer layer. Phase assemblage data along the STO/SrCuO₂ tie line was used to identify possible buffer layer compositions. The composition depended on solubility limits and phase distribution. Compositions off of the tie line were also of interest. These consisted of excess Cu compositions that proved to be conducive to the formation of the low melting temperature phase that promoted liquid phase sintering during thin film synthesis.

Buffer layer design. A new buffer layer for the YBCO coated conductor was designed according to phase assemblage findings and solubility limits established from bulk powder studies. The YBCO coated conductor layer sequence was considered in designing the new buffer layer. Fabrication process optimization calls for only one buffer layer deposited by CSD.

Laboratory setup. A laboratory set up for the fabrication of Cu-doped STO thin films by spin coating was optimized. Small-scale production of thin films in the laboratory environment can be transferred to large-scale production by dip coating. The key elements to consider in the set-up will be reproducibility and control of deposition conditions. An evaluation of the spin coating and deposition set up was conducted in order to assess process efficiency.

Deposition of thin films by spin coating. STO and Cu-doped STO thin films were fabricated on single crystal substrates and on IBAD MgO substrates. The deposition on single crystal substrates allowed for the characterization of the thin films and for the optimization of spin coating parameters prior to extending the results to the coated conductor layered structure. The extent of Cu doping was varied according to the solubility limits. Single layer as well as multi-layer films were deposited, although it was a goal of this research to incorporate only one buffer layer into the YBCO coated conductor structure. Thin films were characterized by atomic force microscopy (AFM), x-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) to evaluate film quality and effects of deposition parameters.

Evaluation of deposition techniques. The STO and Cu-doped STO thin films on IBAD MgO were used as the basis for YBCO coated conductors. YBCO coated conductors with the STO and Cu-doped STO buffer layers were fabricated by PLD and CSD. IBAD MgO substrates were obtained from the Superconductivity Technology Center IBAD team for the deposition of Cu-doped STO buffer layers. Following the deposition of the buffer layers, the YBCO conductor was deposited onto the buffer layer by the method of PLD by the

Superconductivity Technology Center PLD team. Superconductivity properties such as T_c , I_c , and critical current density (J_c) were evaluated for comparison of physical and chemical deposition methods.

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DEPOSITION TECHNIQUES FOR $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ COATED CONDUCTOR ARCHITECTURES

If you do something once, people will call it an accident. If you do it twice, they call it a coincidence. But do it a third time and you've just proven a natural law.

— Grace Murray Hopper (1906–1992)
US military leader, mathematician, educator. She was
co-inventor of the computer language COBOL and coined the term “bug.”

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2.1 ABSTRACT

A common approach for the fabrication of coated conductors employs several vacuum-based deposition techniques such as ion beam assisted deposition (IBAD) and pulsed laser deposition (PLD). These physical vapor deposition (PVD) methods place constraints on high deposition rates, composition flexibility, thin film thickness, and uniform coverage of varying geometries. This chapter reviews the principles of physical deposition methods and alternative chemical solution deposition (CSD) methods such as sol-gel processing and chelate deposition that do not require vacuum conditions.

2.2 INTRODUCTION

The basis for coated conductors is a flexible metallic substrate, mandating a flat, tape-like geometry. Centimeter sized $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) coated conductors are fabricated in the research laboratory setting in a matter of a few minutes to hours. Large-scale application of these coated conductors depends on the economical production of long lengths that maximize the critical current density (J_c) of the superconducting film by minimizing the nonsuperconducting cross-section (1). The production of long lengths of coated conductors is still in the research stage, as typical laboratory deposition rates must be increased by four orders of magnitude to achieve economical fabrication (2). An effective deposition process optimizes superconducting properties by allowing for an increase in the film thickness while coating both sides of the flexible metallic substrate (1, 2). Physical deposition methods such as pulsed laser deposition (PLD) and ion beam assisted deposition (IBAD) requiring high vacuum conditions are more expensive when compared to chemical solution deposition (CSD) techniques that can be carried out at atmospheric pressure. CSD techniques also offer the option of coating multiple or irregular surfaces whereas PLD and IBAD cannot be easily adapted to such deposition constraints. Furthermore, the overall operation of thin film growth by solution means requires less equipment which translates into lower initial capital investments and a process that is less expensive to maintain (3).

Coated conductors are characterized by multi-layer architectures with each layer serving a specific purpose in the structure (Figure 2.1 (4)). The number of layers is not fixed and may be modified to achieve desired properties. The layers can be classified into four categories: the substrate, intervening buffer layer(s), the superconducting film, and a passivating layer for corrosion protection. For coated conductors, the substrate is a flexible metallic substrate with a thickness of approximately 25-100 μm . Substrate lattice parameters must be similar to those of the buffer layer(s) and the superconducting film to promote biaxial growth, growth with in-plane and out-of-plane texture. Thermal expansion coefficients of the substrate must be compatible with those of subsequent buffer layers and the superconducting film

Figure 2.1 The film architecture for YBCO coated conductor tapes developed at Los Alamos National Laboratory uses a polycrystalline Ni-based super-alloy substrate, a Y_2O_3 buffer layer followed by a second IBAD MgO buffer layer. A third buffer layer and the final YBCO are deposited by PLD. A final layer of silver is added for corrosion protection. (4)

to enhance buffer layer adhesion. The substrate material is subjected to the entire coated conductor manufacturing process, which consists of cleaning and deposition of several thin films at varying temperatures and atmospheres. The substrate must exhibit chemical and thermal stability throughout the various deposition process conditions.

Oxide buffer layers play a central role in the coated conductor architecture. Buffer layers transfer the biaxial texture from the substrate or template to the YBCO superconducting film. It is imperative that both the lattice parameter and the coefficient of thermal expansion of the buffer layer match that of the neighboring substrate and the YBCO film to provide mechanical stability and good adhesion. Buffer layers must be smooth, dense, and non-reactive when placed in direct contact with the YBCO. Dense buffer layers provide a two-fold barrier for cation diffusion from the metal substrate to the YBCO film and for oxygen diffusion. YBCO poisoning by Ni cations to a level as low as 3% has been found to reduce the critical superconducting temperature (T_c) to below 77 K (5). Oxide diffusion is faster when compared to cation diffusion in most coated conductors (6). The multi-layer structure of the coated

conductor and the required sequential fabrication scheme exposes the entire composite to varying oxygen atmospheres and temperatures as high as 900°C. Metal oxides may form at the interfaces and affect continuous epitaxial growth, oriented growth transferring from one layer to the next (6). This may be alleviated by depositing a thin layer of an oxide film, such as Y_2O_3 , that can be grown in low oxygen partial pressures directly onto the metal substrate (7). The total thickness of the buffer layers is between 50-200 nm compared to a YBCO total thickness of 1-5 μm (8). Despite the considerable differences in layer thickness, over 20% of the total coated conductor fabrication cost is attributed to buffer layer deposition by vacuum techniques (6).

2.3 EXPERIMENT

PLD and CSD were used to deposit SrTiO_3 (STO) and copper (Cu) doped STO buffer layers on IBAD magnesium oxide (MgO) substrates. A layer of YBCO was deposited onto the buffer layers by PLD to assess microstructural features arising from the different buffer layer deposition techniques. Emphasis was placed on understanding of the deposition techniques used. The details of the deposition processes are given in the following chapters.

2.4 PHYSICAL FABRICATION METHODS FOR COATED CONDUCTORS

2.4.1 Metal Substrate Preparation

Coated conductor fabrication starts with the preparation of a biaxially textured substrate or surface on a polycrystalline substrate material in order to promote biaxial texturing of the subsequent buffer layer and superconducting films. Biaxial texturing refers to a condition of both in-plane and out-of-plane texture. Texturing of the entire substrate is accomplished by the Rolling Assisted Biaxially Textured Substrate (RABiTS) process that forces a texture on the substrate. A face centered cubic (fcc) metal is preferred due to its unique, well-defined

$\{100\}\langle 100\rangle$ texture (6). This cube texture corresponds to a cube plane parallel to the plane of the metal substrate.

The RABiTS process forces the substrate material to take on a $\{100\}\langle 100\rangle$ texture by hot rolling and annealing (9-11). The substrate material preference for RABiTS is high purity nickel. In contrast to the RABiTS process, IBAD produces a biaxially textured substrate by forcing a preferred texture on the first buffer layer (Figure 2.2). The surface texture is then independent of the texture of the underlying metallic substrate, which in this case is a polycrystalline nickel based alloy. The buffer layer is deposited by vapor phase deposition directly onto the randomly oriented substrate. As the buffer layer is being deposited, an ion beam impinging on its surface promotes growth in the $\{100\}$ direction. Preferred orientation throughout the superconducting multilayer structure is independent of substrate texture. In the case of IBAD, the initial buffer layer serves as the textured foundation for deposition of additional buffer layers and the superconducting film. A schematic illustration of the IBAD

Figure 2.2 Schematic of the IBAD process illustrating thin film deposition from a target material guided by an ion assist gun to achieve biaxial texture.

influence on buffer layer texture is presented in Figure 2.3. Metal substrate preparation for a coated conductor structure is beyond the scope of this work, but is introduced to familiarize the reader with the basic processes. All metal substrates were obtained from the Coated Conductor Research Group at Los Alamos National Laboratory. IBAD MgO was used to achieve the required texture.

2.4.2 Buffer Layer and Superconducting Film Deposition

Following the initial processing of the substrate material by either RABiTS or IBAD, the buffer layers and the superconducting film are deposited by PLD (Figure 2.4). PLD produces a thin film by striking a target with a laser source and vaporizing or ablating the target material onto a substrate. The target is a 0.25 inch thick pressed powder disc prepared by conventional ceramic powder processing techniques. Deposition conditions for YBCO are 900°C in a low pressure O_2/N_2 atmosphere.

Figure 2.3 Schematic comparing thin film texture for the conditions of deposition without an assisted beam and for ion-beam assisted deposition. (a) For a single crystal substrate, deposition without an ion-assisted beam will result in a single crystal thin film that grows with the same orientation as the substrate. (b) For a randomly oriented polycrystalline substrate, deposition without an ion-assisted beam will result in a randomly oriented polycrystalline film. (c) For deposition on a randomly oriented polycrystalline substrate with an ion-assisted beam, the resulting thin film will grow in the direction guided by the beam. Biaxial texturing refers to both in-plane and out-of-plane alignment.

Figure 2.4 Diagram of the PLD operation.

Film nucleation and growth resulting from PLD deposition are attributed to three distinct growth modes that are dependent on the thermodynamics relating the surface energies of the film and the substrate and on the film-substrate interface energy (12). The Volmer-Weber nucleation and growth theory predicts three-dimensional island growth when the sum of the free energies between the cluster/vapor and substrate/cluster is greater than the free energy associated with substrate/vapor interface. Two-dimensional full monolayer growth (Frank-van der Merwe) results when the free energy of the substrate/vapor interface is greater than that of the cluster/vapor and substrate/cluster interfaces. In this growth mode clusters of islands still nucleate and grow, but only to a thickness of one monolayer. Complete coalescence is required for additional clusters to form the next monolayer. The Stranski-Krastinov nucleation and growth theory combines the Volmer-Weber and Frank-van der Merwe theories. Thin film formation occurs by two-dimensional growth of full monolayers followed by nucleation and growth of three-dimensional islands after 1-5 monolayers have been deposited.

2.5 THIN FILM PRECURSORS

The deposition source for PLD is a bulk powder target prepared by solid state reaction methods in which metal oxides or carbonates are mixed and fired at high temperatures to allow interdiffusion of the cations. The interdiffusion of cations is affected by the degree of mixing of the inhomogeneous starting mixture that consists of particles ranging in size from 1-10 μm . For a starting mixture of components AO and BO_2 , the solid state reaction occurs at the contact points between AO and BO_2 and proceeds by interdiffusion of the constituents through the byproduct ABO_3 . Continued growth of the byproduct slows the reaction as the diffusion paths increase. Repeated cycles of grinding and firing are required to allow for complete reaction and elimination of unwanted secondary phases. Multiple intermittent grinding and firing can still yield poor sintering, non-uniform particle sizes and shapes, secondary phases, and loss of stoichiometry. In contrast, liquid precursors allow for more precise chemistry control and have a higher degree of homogeneity. Thin films originating from liquid precursors tend to be homogeneous and do not require repeated thermal processing cycles (13, 14).

2.6 CHEMICAL FABRICATION METHODS FOR COATED CONDUCTORS

Similar to coated conductors fabricated by physical methods, the substrate for chemical fabrication is a 0.25 μm thick flexible nickel alloy substrate prepared by RABiTS or IBAD. The buffer layers and the superconducting film are processed by CSD. CSD techniques can be divided into three branches of solution preparation processes depending on the reagents used: sol-gel processes (15), chelate processes (14), and metallorganic decomposition (MOD) (16). Chelate processes and MOD are modifications of the basic sol-gel process. The starting reagents for sol-gel and chelate processes are typically water reactive while those required for MOD are usually water-insensitive. The current study focused on the deposition of a buffer layer by chelate processing. The discussion of specifics of the MOD

process is beyond the scope of this dissertation. Several investigations that address aspects and applications of MOD techniques are available in current literature (17-19).

Regardless of the process utilized, the first step in thin film fabrication is the preparation of a precursor solution. The precursor solution is deposited onto a substrate either by spin coating for smaller samples or by dip coating for larger surface areas. The deposited film is converted into an amorphous film by a low temperature heat treatment in the range of 200-400°C. Transformation from the amorphous state to a crystalline state is achieved by thermal processing at temperatures ranging from 600-1100°C.

2.6.1 Sol-Gel Processes

Prior to the discussion of sol-gel chemistry, several terms must be introduced. A colloid is a suspension with a small dispersed phase (~1-1000 nm) that is unaffected by gravity and that interacts by short-range forces such as van der Waals attraction and surface charges. A colloidal suspension of solid particles in a liquid is referred to as a sol. Sol-gel processing requires the preparation of a colloid using precursors that consist of a metal or metalloid element surrounded by ligands. A ligand is an appendage that does not consist of a metal or metalloid atom. The most widely used precursors are metal alkoxides due to their reactivity with water. Metal alkoxides are referred to as $M(OR)_n$ where M is a metal, n is the metal valence, and R is an alkyl group. An alkane is a molecule containing only carbon and hydrogen linked by single bonds, for example methane CH_4 . An alkyl is a ligand formed by removing one hydrogen from an alkane molecule, for instance methyl ($\bullet CH_3$). An alcohol is a molecule formed by adding a hydroxyl (OH) group to an alkyl (or other) molecule. An alkoxy is a ligand formed by removing a proton from the hydroxyl on an alcohol.

Sol-gel processes for the deposition of perovskite materials are mainly based on the use of 2-methoxyethanol ($CH_3-OCH_2CH_2OH$) as the solvent due to its ability to solubilize a variety of starting reagents, although other alcohols have been utilized (15). The key reactions in this CSD process are:

Hydrolysis is the partial or complete reaction of the metal alkoxide with water during which a hydroxyl ion attaches to the metal atom. Following hydrolysis, condensation links hydrolyzed molecules together to liberate alcohol (Equation 2.2) or water (Equation 2.3) molecules. Polymerization, the formation of larger metal containing molecules, occurs as condensation proceeds. Monomers are the building blocks of polymers that are capable of forming a minimum of two bonds. Once the two-bond limit is exceeded, the molecule can grow into a gel, a macroscopic molecule that extends throughout the solution.

2.6.2 Chelate Processes

Chelate processes are based on the molecular modification of alkoxide compounds through reactions with other reagents such as acetic acid or acetylacetone (acac, 2,4-pentanedione) (14, 20). Chelating agents reduce the hydrolysis sensitivity of alkoxide compounds. For these specific processes the most widespread reagent is acetic acid. Chelate processing routes, like sol-gel processing, involve hydrolysis and condensation reactions for the formation of the precursor solution. However, in this case the key reaction is the chelation of the metal alkoxides. For acetic acid:

Solution aging is a detrimental characteristic of precursors in the chelate process. With time (weeks to months depending on the particular solution) precursor solution characteristics change due to continued esterification of the solution that leads to the formation of precipitates (20). This problem can be avoided by minimizing the storage life of precursor solutions.

2.7 SPIN COATING

Thin film deposition is one of the key technological applications of chemical solution deposition. This can be accomplished through various means such as dip coating, spin coating, or spraying. Dip coating and spraying are more applicable to industrial processes requiring reel-to-reel continuous deposition. Dip coating involves a continuous process of immersing and drawing the substrate from a precursor solution under controlled conditions, i.e. immersion/drawing speed. Fabrication of long lengths of coated conductors requires that each stage in the deposition process be scalable. Spin coating is appropriate for the research lab setting since the operation is based on small substrate sizes ($\sim 1\text{mm} \times 1\text{mm}$). Spin coating involves the acceleration of an excess of liquid (a liquid puddle) on a rotating substrate. The four basic stages of the spin coating operation are deposition, spin-up, spin-off, and evaporation (Figure 2.5) (21).

2.7.1 Spin Coating Stages

Stage I Precursor Deposition. An excess of precursor solution is dispensed onto the substrate using a syringe or an automatic dispenser. Sub-micron size filters may be used to trap particles that could result in surface flaws as shown in Figure 2.6 (22). Substrate surfaces should be free of any contamination to permit complete wetting of the surface by the precursor solution. Depending on the nature of the substrate, the surface may be cleaned with an etchant or sprayed with an inert gas to remove residues.

Stage II Spin-up. Film deposition occurs by accelerating the substrate to a predetermined rotation speed by making appropriate adjustments to the spin coating unit. Rotational motion causes aggressive fluid expulsion from the substrate. Centrifugal forces dominate over gravity and other inertial forces causing flowing and thinning of the liquid in a radial pattern. Due to the excess of fluid dispensed onto the substrate, spiral vortices may result due to the inertia that the top of the fluid layer exerts while the underlying substrate accelerates. At

Figure 2.5 Schematic illustrating the stages of the spin coating process. (a) Deposition refers to an amount of precursor solution dispensed onto the surface of the substrate. (b) During spin-up the substrate is accelerated to a predetermined speed to remove excess precursor solution from the substrate and form a uniform film. (c) During spin-off, fluid film thickness decreases due to the influence of viscosity forces. (d) Evaporation of volatile solution components dominates the final film thinning behavior. (21)

a critical fluid thickness, a uniform film of fluid rests on the substrate and co-rotates with the substrate.

Stage III Spin-off. The spinning motion of the substrate promotes further thinning of the fluid film dominated by viscous flow effects. Fluid thinning tends to be uniform but edge effects may be observed because as the fluid flows outward it forms droplets at the edge to be flung off. Solutions containing volatile solvents exhibit interference colors spinning off as the fluid film thickness decreases. During spin-off, a film of fluid tends to become uniform and will remain so providing that the liquid exhibits Newtonian viscosity that remains constant throughout the surface of the substrate (23). This behavior is prevalent due to the balance between centrifugal forces that drive the flow radially outward and viscous forces that pull the flow radially inward (24). As the spin-off stage nears completion, resistance to

Figure 2.6 SEM micrographs showing “comet” surface defects on the surface of silica-titania on silica. These defects are typical of the presence of particulates on the surface of the substrate prior to solution dispense or of unfiltered precursor solutions. (22)

flow increases due to a decreased film thickness and due to an increased viscosity resulting from a greater concentration of nonvolatile components in the thinner film.

Stage IV Evaporation. As the substrate continues to spin at a constant rate and the fluid thins, viscosity effects are negligible compared to solvent evaporation. The evaporation of volatile solvent species dominates the coating behavior. Further thinning by fluid flow is limited as volatile solvents evaporate causing a rise in the viscosity that gels the fluid onto the substrate.

The breakdown of the spin coating operation into four stages is for process dynamics simplification. Stages III and IV, spin-off and evaporation, occur simultaneously. They are separated to illustrate that viscous flow effects dominate until the thickness of the fluid decreases to a certain point at which evaporation controls the thinning behavior.

Following the spin coating operation, the thin films may undergo a pyrolysis step to dry the film. This is accomplished at low temperatures ($\sim 200\text{-}300^\circ\text{C}$) for a few minutes either on a hot plate exposed to ambient conditions in a hood or in a tube furnace with a controlled environment. The choice of using a hot plate or a tube furnace is dictated by the parameters that optimize the thin film quality for a particular material system.

2.7.2 Viscous Fluid Flow on a Rotating Disk

The origins of spin coating modeling date to 1958 with the publication of findings by Emslie, et al. on the modeling of flow of a viscous fluid rotating on a disk prompted by an interest on thin film deposition on color television screens (25). The analysis of fluid flow on a rotating disk was made on a series of assumptions: (1) the rotating plane is infinite in extent; (2) the plane is horizontal, so that there is no radial gravitational component; (3) the liquid layer is radially symmetric, and so thin that differences in gravitational potential normal to the surface of the disk have a negligible effect in distributing the liquid compared with the effect of centrifugal forces; (4) the viscosity is independent of the rate of shear, i.e. the liquid is Newtonian; (5) the liquid layer is everywhere so thin that shear resistance is appreciable only in horizontal planes; (6) the radial velocity is everywhere so small that Coriolis forces may be neglected. Assuming that fluid flow has reached a stable condition where centrifugal and viscous forces are in balance (the spin up stage is excluded) and assuming a cylindrical coordinate system aligned with the axis of substrate rotation and where the angular velocities ω_θ and ω_z are zero, the r component of the equation of motion in terms of the viscous shear stress, τ , (26) may be simplified to:

$$\rho\omega^2 r = \frac{\delta\tau_{rz}}{\delta z} \quad (2.5)$$

where r is the radius of the spinning layer of fluid. Figure 2.7 shows a schematic of the thin film geometry. Newton's law of viscosity can be used to obtain an expression for the balance of viscous and centrifugal forces:

$$\tau = -\mu \frac{\delta v_r}{\delta z} \quad (2.6)$$

$$\rho\omega^2 r = -\mu \frac{\partial^2 v}{\partial z^2} \quad (2.7)$$

where μ is the viscosity of the fluid in poise. Equation (2.7) may be integrated with the boundary conditions that $v=0$ at $z=0$ (the surface of the disk) and $\frac{\delta v}{\delta z} = 0$ at the $z=h$, the free surface of the liquid where the shearing force vanishes,

Figure 2.7 Side view of the spinning disk. The disk rotates about the z -axis with angular velocity, ω_r . The liquid free surface defined by $z=h$ is a function of radial position r and time t . (21)

$$v = \frac{1}{\mu} \left(-\frac{1}{2} \rho \omega^2 r z^2 + \rho \omega^2 r h z \right) \quad (2.8)$$

The radial flow q per unit length of circumference is given by the integration of the velocity distribution (equation 2.8)

$$q = \int_0^h v dz = \frac{\rho \omega^2 r h^3}{3\mu} \quad (2.9)$$

An equation for h , the final film thickness, can be obtained by applying the equation of continuity for cylindrical coordinates (26). Assuming conservation of mass, the change in height of the fluid, $\frac{\delta h}{\delta t}$, varies as the flux of material, $\frac{1}{r} \frac{\delta}{\delta r}(rq)$, out of the circular boundary.

$$r \frac{\delta h}{\delta t} = - \frac{\delta(rq)}{\delta r} \quad (2.10)$$

Combining equations (2.9) and (2.10) gives

$$\frac{\delta h}{\delta t} = -K \frac{1}{r} \frac{\delta}{\delta r}(r^2 h^3) \quad (2.11)$$

where $K = \frac{\rho \omega^2}{3\mu}$

Equation 2.11 has a special solution that depends only on t .

$$\frac{dh}{dt} = -2Kh^3 \quad (2.12)$$

where h_0 is independent of r and corresponds to the initial height of the fluid film at time $t=0$. Equation 2.12 can be integrated to obtain an equation for h ,

$$h = \frac{h_0}{(1 + 4Kh_0^2 t)^{\frac{1}{2}}} \quad (2.13)$$

Equation 2.13 sets the condition that at $t=0$, the fluid has an initial uniform distribution, $h=h_0$. If the initial fluid distribution is uniform throughout, it will remain so with time as the thickness of the fluid film decreases due to centrifugal forces. If the initial thick film

distribution can be made uniform before centrifugal forces take effect, then film uniformity is guaranteed. If the initial fluid distribution is not uniform, then uniformity cannot be predicted.

Equation 2.13 gives the thinning rate for the early stages of fluid thinning governed by viscosity influences. However, other considerations must be made during stage IV of the spin coating operation where solvent evaporation dominates fluid thinning behavior. Meyerhofer (27) was the first to evaluate the effect of solvent evaporation on final coating thickness. He speculated that if the rotation rate is held constant, evaporation is constant throughout the spinning operation. This can be accounted for by adding a constant evaporation term, e in $\text{mL} / \text{s cm}^2$, to equation 2.13.

$$\frac{\delta h}{\delta t} = -2Kh^3 - e \quad (2.14)$$

Solution of an expression for the final coating thickness, h_f , incorporated the assumptions that early spin coating stages (stages II and III) are controlled by viscous flow and later stages (stage IV) are controlled by evaporation. The transition point was set at the condition where the viscous flow rate and the evaporation rate are equal. The final coating thickness was predicted to be

$$h_f = c_o \left(\frac{e}{2(1 - c_o)K} \right)^{\frac{1}{3}} \quad (2.15)$$

where c_o is the solids concentration in the solution. Research has shown that the evaporation rate should be constant over the entire substrate and depends on the rotation rate according to

$$e = C\omega^{\frac{1}{2}} \quad (2.16)$$

where C is a proportionality constant that is determined for the specific experimental conditions. The square root dependence arises from diffusion being the rate-limiting step

through a vapor boundary layer above the spinning disk. It is assumed that the airflow above the spinning substrate is of a laminar nature.

2.7.3 Thin Film Crystallization: Gel to Ceramic Transformation

The standard theory of crystallization in glasses can be applied to the nucleation and growth behavior of thin films. Analysis of thin film crystallization is beyond the scope of this dissertation. An excellent discussion of crystallization in glasses can be found in references 28-31.

2.8 CHEMICAL SOLUTION DEPOSITION—CURRENT TECHNOLOGY

The current methods for coated conductor substrate fabrication are IBAD and RABiTS. IBAD is capable of yielding meter long coated conductor tapes with uniform properties. Whether the IBAD process can be scaled up to produce longer lengths with uniform properties while remaining cost effective, is still unclear. The RABiTS technique can produce tens of meters of coated conductor lengths; scale up possibilities of this process are more promising than for the IBAD technique. The use of the IBAD method for substrate texturing is accepted. However, the deposition of subsequent buffer layers and YBCO by PLD is in question. The future of coated conductor industrial applications is dependent on the development of deposition techniques that are scalable, less complicated, and economical. Based on these stringent conditions, processing techniques relying on wet chemistry are promising alternatives.

CSD techniques have focused on the deposition of thin films on single crystal substrates. Several process limitations have been identified (33). The oxidizing heat treatment conditions that are required to thermally process deposited thin films are not favorable for the textured metallic substrates called for by coated conductors. High thermal processing temperatures may oxidize the nickel alloy substrates. Solution stability presents yet another problem due

to limited solution shelf life that results from the precipitation of solutes in the precursor solution. Depending on the nature of the substrate used for spin coating, non-uniform surface wetting may result, leading to the formation of isolated islands on the films yielding non-uniform film thicknesses. In some instances, seed layers are required to obtain textured films. The use of a seed layer increases the thin film processing time and the costs associated with CSD.

Spin coating is a laboratory scale thin film deposition process that is well suited for the fabrication of small samples. There are several advantages of spin coating over other deposition processes (33, 34). The degrees of freedom in the process are spin speed, spin duration, and solution viscosity. Film thicknesses can be modified by altering these three parameters. Moreover, thin films progressively achieve uniformity as the film thins during the spinning operation. Once the film becomes uniform during the coating process, it will remain so for the entire duration of the process (25).

Disadvantages of the spin coating operation may be summarized as follows (34, 35). Spin coating is not adaptable to large-scale fabrication operations. Large substrates cannot be spun at required high rates in order to allow the film to thin and dry in a timely manner. Spin coating may be used in a laboratory setting to optimize deposition conditions that may then be extended to the process of dip coating for large-scale production. Only 2-5% of the solution dispensed onto the substrate forms the actual thin film; the remaining 95-98% is flung off of the surface of the substrate during the coating process (335). Over 95% of the photoresist solutions are wasted and have to be disposed of as toxic materials. The cost of raw organic materials used to make the required solutions are substantial and so are the associated disposal costs. The disadvantages associated with spin coating are minimal when it is considered that the operation is a laboratory scale process that only requires small samples as well as small chemical volumes.

2.9 CHEMICAL SOLUTION DEPOSITION OF YBCO SUPERCONDUCTORS AND STO BUFFER LAYERS

Research trends in superconductivity have focused on the development of viable processing techniques that yield high quality thin films without compromising superconducting properties. Deposition of YBCO superconductor and STO (buffer layer) thin films has been achieved by a variety of vacuum (CVD, PLD, IBAD) and nonvacuum techniques (CSD). CSD techniques such as MOD methods have several advantages over vacuum deposition routes. The main operational advantages are rapid deposition rates and the ease with which films of uniform and controlled composition can be prepared. In addition, CSD does not require sophisticated vacuum systems, which give the technique an economic edge over physical deposition processes.

Preparation of bulk YBCO superconductors with a critical temperature of approximately 90 K is routine when compared to the preparation of thin films with such high transition temperatures. Early YBCO thin films prepared by MOD involved the use of metal carboxylates (36). Chen et al. reported that YBCO films prepared from metal carboxylate precursors had poor electrical properties due to the formation of BaCO_3 , an intermediate compound that forms during the decomposition of the precursors. Sustained heating above 800°C eliminates the BaCO_3 phase but results in a reaction between the film and the substrate. Gupta et al. (37) and McIntyre et al. (38) later reported that the use of fluorinated precursors like metal trifluoroacetates (TFA) does not yield the unwanted BaCO_3 phase. For the TFA method, yttrium, barium, and copper trifluoroacetates decompose in oxygen to oxyfluorides. These are then converted to oxides through exposure to a humid furnace atmosphere. Gupta reported a zero-resistance transition temperature slightly higher than 90 K. McIntyre documented zero-field critical current densities in excess of 10^6 A/cm^2 at 77 K.

Sathyamurthy et al. (39) built an YBCO coated conductor by using an acetate based MOD process to deposit thin film buffer layers on single crystal substrates followed by a TFA process to deposit the YBCO film. The coated conductor consisting of an YBCO/STO

combination resulted in transition temperature of 90-91 K and critical current densities of the order of 10^5 A/cm² at 77 K and self-field. Rupich et al. employed a combination of RABiTS and MOD to produce an YBCO coated conductor with a critical current greater than 4 MA/cm² (40).

While it is of great significance to be able to manufacture a coated conductor exhibiting a high critical current at high temperatures, the basic interaction of the series of layers making up the conductor structure must not be ignored. The buffer layers, or the layers in between the substrate and the superconductor, take on the critical role of serving as a template for the preferred orientation of YBCO while chemically isolating it from the substrate. With this in mind, numerous studies have been centered on the chemical solution deposition of buffer layers, such as STO (41, 42). Ceramics such as YSZ, CeO₂, MgO, BaZrO₃ can be used as buffer layers for the YBCO coated conductor, however, STO is the best known substrate for YBCO. Research on CSD of STO has thus far shown that thin film texture is independent of the furnace atmosphere (39), higher ramp rates during post pyrolysis heat treatment yield denser films (41), the addition of acetylacetone to the precursor solution results in denser films with a fine microstructure (42), and the initiation of STO crystallization occurs at temperatures above 550°C (42-44). Further investigations are needed to develop reliable and reproducible correlations between the properties of the STO thin film and deposition conditions.

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THE SrO-CuO-TiO₂ TERNARY PHASE SYSTEM: AN INDICATION OF COPPER AFFINITY IN THE SrTiO₃ STRUCTURE

*One never notices what has been done;
one can only see what remains to be done . . .*

— Marie Curie (1867–1934)
Polish-French chemist. She was renowned
for her work on radioactivity and discovering polonium and radium.

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3.1 ABSTRACT

The microstructural progression of bulk powder SrTiO₃ (STO) with increasing levels of copper (Cu) processed at 1050°C in 10% oxygen partial pressure (P(O₂)) and 100% O₂ atmospheres for 200 hours was studied. X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) were used to evaluate the phase assemblages and solubility limits of Cu in STO. Both processing atmospheres increased the porosity of the bulk samples and yielded secondary phases as Cu concentration levels increased. XRD analysis showed that Sr(NO₃)₂, an artifact of processing, was present in the bulk powders. The maximum solubility limit of Cu in STO was found to be 1%. The results of this work will be submitted for publication. The research collaborators were T.G. Holesinger, W. Wong-Ng, L. P. Cook, Q.X. Jia, and J.A. Kennison.

3.2 INTRODUCTION

The successful development and application of buffer layers for the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) coated conductor structure is dependent upon controlled processing conditions that can be tailored to yield desirable material characteristics. SrTiO_3 (STO) is a potential buffer layer candidate in the YBCO coated conductor structure because the lattice misfit between STO and YBCO is only $\sim 1.5\%$. Numerous studies have focused on the deposition of YBCO on various substrates, but few have studied the deposition on variations of the STO compound. The interaction of STO with YBCO is of interest if the two materials are to be used in a coated conductor composite. Several investigations have shown that STO/YBCO interactions change depending on the deposition conditions. Wang et al., have shown that by changing the STO deposition temperature the critical current density (J_c) can be varied over a large range (1). The J_c of YBCO films increases from 1 MA/cm^2 to 3 MA/cm^2 as the deposition temperature of STO increases from 670°C to 820°C , but drops to 0.9 MA/cm^2 as the STO deposition temperature further increases to 860°C . Others have shown that one or more secondary phases are found at the interface of the YBCO and STO layers at deposition temperatures above 850°C (2). Prior to addressing the STO/YBCO compatibility issue, phase information for STO or STO variations must be known.

Processing of the various components of the coated conductor is accomplished either by thin film deposition through the use of bulk powder ceramic targets or by chemical solution techniques. In the process of combining several materials to produce a composite structure, knowledge of the material system at hand is crucial to the determination of optimum fabrication parameters. Phase diagrams are essential tools that outline the temperature-dependent composition of a material system. Phase diagrams (i.e. equilibrium diagrams or constitution diagrams) define the stability regions and solubility limits of the phases that can occur in a system of materials at a specified temperature and pressure. A phase is defined as a portion of the system whose properties and composition are homogeneous and which is physically distinct from other parts of the system (3). One of the stipulations of phase

diagrams is that the interacting materials must be in a state of equilibrium. Non-equilibrium phases or metastable phases resulting from treatments such as quenching (rapid cooling) cannot be incorporated into equilibrium phase diagrams because with time and appropriate amounts of motion induced by thermal activity, the metastable states can be driven to equilibrium. This chapter addresses phase assemblage in the STO/SrCuO₂ binary system by reporting the microstructural evolution of a series of ceramic powders heat treated to high temperatures and quenched in liquid nitrogen to preserve the high temperature phase assemblage. The solubility of copper (Cu) in the STO structure was of significant importance to this research.

The atmosphere that a material is exposed to during heat treatments also affects the phases present in a given system under specified conditions. An atmosphere of 100% O₂ vs. one of 10% O₂ / 90% Ar or some other combination of noble gases may favor the formation of two or more distinct phases. It was the intention of this research to address the possible effects of oxygen partial pressure (P(O₂)) on the resulting microstructure of samples of varying composition. It was assumed that featured microstructures were in a state of equilibrium when multiple x-ray diffraction (XRD) analysis following regrindings and heating gave the same XRD spectra.

3.3 EXPERIMENT

The materials used for bulk powder preparations were reagent grade 99.999% pure SrCO₃, CuO, and TiO₂ (Alfa Aesar). The compositions of the bulk powders prepared ranged from x=0 to x=1 for Cu in Sr₁Cu_xTi_{1-x}O_y. The compositions for determination of the solubility limits ranged from x=0 to x=0.2 in Sr₁Cu_xTi_{1-x}O_y (Table 3.1).

Phase pure STO and SrCuO₂ powders were required for quantitative compositional analysis. The two standards were prepared by mixing calculated proportions of the starting materials in isopropanol in an automatic mortar and pestle for 4 hours. The solution was dried on a schlenk line (vacuum line) using liquid nitrogen traps to collect the liquid. The STO standard was treated at 900°C for 10 hours, followed by 2 additional treatments at

Table 3.1. Summary of Compositions of Cu-substituted STO Bulk Powder Samples Prepared with Varying Cation Ratios.

Sample	Sr (% x 100)	Cu (% x 100)	Ti (% x 100)
SrTiO ₃ standard	1	-	1
1	1	0.03	0.97
2	1	0.05	0.95
3	1	0.075	0.925
4	1	0.10	0.90
5	1	0.13	0.87
6	1	0.15	0.85
7	1	0.17	0.83
8	1	0.20	0.80
9	1	0.50	0.50
10	1	0.20	0.90
SrCuO ₂ standard	1	1	-

1050°C (10 hours each). The SrCuO₂ standard was treated at 800°C for 10 hours followed by 2 additional treatments at 1050°C (each for 10 hours).

The remaining bulk powder batches were dissolved on low heat in a dilute nitric acid solution (100 mL nitric acid, 500 mL distilled H₂O) and mixed for 12 hours or until the solution attained a deep turquoise color. The drying process was carried out on a schlenk line cooled by liquid nitrogen. Once the powder was dry, it was maintained under vacuum for an additional two hours at low heat. The dried powders were ground and fired in an alumina crucible at 600°C in air for 5 hours to remove any remaining traces of the nitrates. The powders were ground and pressed into 1-inch pellets for thermal processing and then were processed several times in an alumina crucible with intermittent grindings and pressings for complete reaction. One heat treatment was carried out at 1050°C in oxygen for a total of 200 hours. A small amount of this powder was used to press two 0.5-inch pellets. The pellets were treated at 1050°C for 50 hours, one at 10% O₂, 90% Ar and the other at 100% P(O₂). All samples were quenched in a liquid nitrogen bath held at ambient conditions.

The pellets were sectioned using a slow speed diamond saw and prepared for analysis. A portion of the pellet was ground to a fine powder for XRD analysis to determine the phases present in the resulting powders. XRD analysis was performed with a SCINTAG

Diffractionmeter using Cu K $_{\alpha}$ radiation for the θ -2 θ scans. Samples for scanning electron microscopy (SEM) were prepared by cold mounting a section of the pellet in a 1.5" resin mount. The surface of the mount was ground using 320, 400, 600, 800, and 1200 grit Buehler silicon carbide grinding paper. Diamond paste (Buehler) ranging from 9 μ m to 0.25 μ m size was used for final polishing. A JOEL 6300 SEM operating at 5 KV was used for the microstructural evaluation. Samples for transmission electron microscopy (TEM) were prepared by sectioning off a 3 mm wide portion of the pellet, grinding it down to a cylindrical geometry using 400 grit paper, and then inserting the specimen into a 0.5" long, 3 mm diameter stainless steel tube. A two-part epoxy torr sealTM was used fix the sample in the stainless steel tube. Once the torr sealTM cured (approximately 4 hours), the tubular TEM sample was sectioned into 220 μ m thick slices using a slow speed diamond saw. The individual TEM samples were ground to 110 μ m thickness by grinding on both sides with 400, 600, 800, and 1200 grit Buehler silicon carbide grinding paper. TEM samples were dimple polished on both sides with 3, 1, and 0.25 μ m diamond paste on an SPI Dimpler with a 0.10 μ m diamond suspension as the lubricant (Buehler). Ion milling was performed on a rotating stage with a 3.5 kV beam at a grazing angle of 4° on a Gatan Duo Mill. A Philips CM30 transmission electron microscopy operating at 300 kV was used for TEM analysis.

TEM EDS compositional analysis on individual grains was performed with a size 6 aperture. The magnification was adjusted for each grain to ensure that the beam was focused only on that one grain. A minimum of 10 compositional spectra, at 5 minutes each, were collected for each phase. Phases were recognized by grain geometry. In general, the STO phase with some Cu substitution was square-like while other Cu phases were small and could be found in between larger grains.

The Cliff-Lorimer ratio method (4) was used to quantify atomic percentages of the individual elements in the Cu-substituted powders using the single phase STO and SrCuO₂ powders as standards. Quantitative x-ray microanalysis in electron beam instruments initiated with the study of bulk specimens in which the electron beam is absorbed, as opposed to thin

specimens that transmit the beam. Hillier and Baker were the first to describe the possibility of using x-rays generated by a focused electron beam to give elemental information about the specimen (5). The necessary equipment and the essential steps to obtain quantitative data from bulk specimens were devised in 1951. According to the Cliff-Lorimer method the concentration of an element in a specimen is proportional to the intensity ratio of the measured x-ray intensity emerging from the specimen to the measured x-ray intensity emerging from a chosen standard. A standard of known composition must be chosen due to the difficulty of measuring the intensity of characteristic x-rays generated by an element i in the specimen. The concentration C_i of an element i in a specimen is then given by

$$C_i/C_{(i)} = [K] I_i/I_{(i)} \quad (3.1)$$

where $C_{(i)}$ is the composition of the standard, K is a sensitivity factor that depends on the atomic number (Z), the absorption of x-rays within the specimen (A), and the fluorescence of x-rays within the specimen (F); I_i is the measured intensity emerging from (not generated within) the specimen; and $I_{(i)}$ is the measured intensity emerging from the standard. K takes into account the difference between the generated and the measured x-ray intensities for both the standard and the unknown. For the case of thin electron-transparent specimens required for TEM studies, the absorption and the fluorescence of x-rays can be ignored due to the reduction of sample volume being analyzed. This is referred to as the thin-foil criterion, which assumes that the specimen is thin enough for any absorption and fluorescence of x-rays to make a significant contribution.

The Cliff-Lorimer ratio technique takes equation (3.1) and rewrites it for a binary system, ternary system, and so on assuming that the only necessary data is the ratio of intensities of two elements (4). Intensity data from a standard is not necessary for this analysis. For this research, a ternary system was considered. The Cliff-Lorimer equations are as follows.

Sensitivity Factors

$$K_{(Sr/Ti)} \quad (3.2)$$

$$K_{(Sr/Cu)} \quad (3.3)$$

Specimen Composition

$$C_{Sr} + C_{Ti} + C_{Cu} = 1 \quad (3.4)$$

Concentration Equations

$$C_{Sr}/C_{Cu} = K_{SrCu} (I_{Sr}/I_{Cu}) \quad (3.5)$$

$$C_{Sr/Ti} = K_{SrTi} (I_{Sr}/I_{Ti}) \quad (3.6)$$

$$C_{Sr} = 1/[1 + (I_{Cu}/K_{SrCu} I_{Sr}) + (I_{Ti}/K_{SrTi} I_{Sr})] \quad (3.7)$$

$$C_{Ti} = 1 - C_{Sr} - (C_{Sr} I_{Cu} / K_{SrCu} I_{Sr}) \quad (3.8)$$

$$C_{Cu} = 1 - C_{Sr} - C_{Ti} \quad (3.9)$$

It is of importance to note that there are often large errors associated with quantitative x-ray microanalysis because the thin foil results in few x-ray photons per incident electron when compared to that of bulk specimens. The error associated with this quantification method arises from poor counting statistics. This is alleviated by using higher-brightness sources, large electron probes, thicker specimens, and longer collection times.

3.4 RESULTS

The compositions studied were along the tie line between STO and SrCuO₂ with an emphasis on low %Cu addition (%Cu ≤ 20). The compositions were chosen to illustrate microstructural behavior as the Cu concentration in STO increased. One composition with an excess of Cu was selected to study the behavior of the compound off of the STO/SrCuO₂ tie-line.

3.4.1 Bulk Powder Standards

The overall microstructures of the standards are shown in Figure 3.1. All microstructures shown are depicted by SEM backscattered electron images. SEM EDS analysis confirmed

Figure 3.1 SEM backscattered electron micrographs of the (a) STO and (b) SrCuO_2 standards used in the x-ray quantitative analysis in the TEM. The uniform contrast indicates that both bulk powder samples were single phase in agreement with the XRD results.

the phase purity of the standard materials that were used in the EDS quantification process in the TEM. Figure 3.1(a) and 3.1(b) show the resulting single phase microstructures of the STO and SrCuO_2 standards, respectively. The uniform contrast of the backscattered images indicates phase purity. Comparison of the two standards reveals that in contrast to the dense microstructure of the STO, the SrCuO_2 standard exhibits uniform porosity. In the case of the STO, individual grains of varying grain sizes can be identified, whereas for SrCuO_2 the surface appears smooth and featureless. The cracks that can be seen throughout the microstructure of the SrCuO_2 standard are a result of stresses induced by the metallographic preparation procedure. The XRD data plots in Figure 3.2(a) and 3.2(b), STO and SrCuO_2 respectively, confirm phase purity of the standards.

3.4.2 Microstructural Effects of Varying Oxygen Partial Pressures ($P(\text{O}_2)$)

Figure 3.3 shows the microstructural evolution of three powder batches heat treated at two different atmospheric conditions for 50 hours. The column on the left shows the backscattered image of the powders exposed to a 10% $P(\text{O}_2)$ atmosphere (balance Ar) and the right column depicts the corresponding backscattered images for 100% O_2 thermal

Figure 3.2 XRD data collected for the STO and SrCuO₂ standards. The asterisk (*) in (a) denotes diffraction peaks for the LaB₆ standard used to verify instrument calibration. (a) STO, (b) SrCuO₂.

Figure 3.3 SEM backscattered micrographs of overall microstructures of the three samples after processing at 1050°C in 10% (left column) and 100% P(O₂) (right column). (a) and (b) SrCu_{0.10}Ti_{0.90}O_x; (c) and (d) SrCu_{0.50}Ti_{0.50}O_x; (e) and (f) SrCu_{0.20}Ti_{0.90}O_x.

processing conditions. In general, the pellets exhibited a porous structure at varying levels of Cu concentration.

SEM analysis of the Cu-doped STO samples reveals the microstructural evolution that results as Cu doping levels increase. Small incremental additions of Cu alter the microstructure by promoting the formation of multiple phases as well as increased porosity. For the 10% Cu doped powder, Figures 3.3(a) and 3.3(b) reveal the presence of a secondary phase. The percentage of this secondary phase increased with the higher $P(O_2)$. Corresponding SEM EDS analysis confirmed that this was a Cu-rich phase (lighter area), which was presumed to be $SrCuO_2$. The latter secondary phase was not detected by XRD for either of the $P(O_2)$ processing conditions, indicating that samples of the composition $SrCu_{0.10}Ti_{0.90}O_y$ were composed of one primary phase. The XRD detection limit for secondary phases is 5%. That is, the secondary phase must be at least 5% of the total phases present in order for it to be detected by XRD techniques.

Figures 3.3(c) and 3.3(d) show that, as expected, in the case of $SrCu_{0.50}Ti_{0.50}O_y$ the quantity of secondary phase was much greater than that seen in the lower % Cu powder when processed under the same conditions. SEM EDS analysis showed that this secondary phase was Cu-rich. Results of XRD analysis indicated the presence of STO and a Cu-rich phase resulting from both processing atmospheres. However, at the lower $P(O_2)$ the secondary phase was dispersed throughout the microstructure while segregating the primary phase into a needle-like configuration, the primary phase being STO. The 100% $P(O_2)$ processing atmosphere did not yield this intermixing of the two phases, suggesting that at a lower $P(O_2)$ a more extensive phase segregation will occur.

For $SrCu_{0.20}Ti_{0.90}O_y$, Figures 3.3(e) and 3.3(f) show that small amounts of a Cu-rich phase, presumably $SrCuO_2$, could be found in the matrix. The amount of this phase did not appear to change as a function of the oxygen partial pressure during thermal processing. XRD analysis of this powder did not detect $SrCuO_2$ or any other secondary phases.

3.4.3 Cu-Doped STO Bulk Powders Processed in 100% O₂ Atmosphere

The overall microstructures of the standards and the processed Cu-substituted STO powders with % Cu $\leq$ 20% are shown in Figures 3.4(a)-(j). All microstructures shown are depicted by backscattered electron images. The series of micrographs corresponds to powder samples heat treated at 1050°C for 200 hours in a 100% O₂ atmosphere and quenched in liquid nitrogen. The SEM sequence of the Cu-doped STO samples illustrates a striking microstructural evolution that results with increasing Cu doping levels. Figure 3.4(a) corresponds to the microstructure of the STO standard while Figure 3.4(j) corresponds to that of the SrCuO₂ standard. Small incremental additions of Cu alter the microstructure by promoting the formation of multiple phases as seen in backscattered electron images. A 3% addition of Cu to STO transforms a dense, single-phase microstructure to a multi-phase microstructure characterized by enhanced grain growth. The grain growth phenomenon is seen as the microstructure evolves from low Cu doping to higher Cu concentrations (up to 20% Cu). Comparison of the grain size in the low Cu composition powders (e.g. Figure 3.4(b)) to that of the higher percent Cu (e.g. Figure 3.4(i)) shows enhanced grain growth and densification as the % Cu increases. This suggests the occurrence of liquid phase sintering in the mixture of powders of different chemistries. In this case the starting powders are SrCO₃, TiO₂, and CuO with respective approximate melting temperatures of 2531°C, 1843°C, and 1446°C (6). The equilibrium heat treatment was carried out at 1050°C for 200 hours. Liquid phase sintering enhances interparticle bonding leading to changes in pore structure and densification (7). This explains the behavior exhibited by the bulk samples in the 0% to 20% Cu range. As the Cu concentration increased, liquid phase sintering was encouraged by the higher concentration of the lower melting temperature powder, CuO. Liquid boundary phases were identified in the 10% Cu-doped STO as shown in Figure 3.5. The heat treatment conditions for this sample were 1050°C for 200 hours in 100% O₂ followed by quenching in liquid nitrogen. The 10% Cu doping level seems to be a critical point for the development of a liquid phase that binds the microstructure.

Figure 3.4 SEM backscattered images of bulk powder samples thermally processed at 1050°C for 50 hours in a 100% P(O₂) atmosphere and quenched in liquid nitrogen bath held at ambient conditions. (a) STO, (b) SrCu_{0.03}Ti_{0.97}O_y, (c) SrCu_{0.05}Ti_{0.95}O_y, (d) SrCu_{0.075}Ti_{0.925}O_y, (e) SrCu_{0.10}Ti_{0.90}O_y, (f) SrCu_{0.13}Ti_{0.87}O_y, (g) SrCu_{0.15}Ti_{0.85}O_y, (h) SrCu_{0.17}Ti_{0.83}O_y, (i) SrCu_{0.20}Ti_{0.80}O_y, (j) SrCuO₂.

Such a phase is a critical component of the buffer layer material because it can result in the formation of a smooth interface with minimum porosity. This phenomenon was observed for a sintering duration of 200 hours. The microstructure depicted in Figure 3.6 suggests the increased presence of a lower melting phase as the level of Cu concentration increases. For the $\text{SrCu}_{0.80}\text{Ti}_{0.20}\text{O}_x$ bulk powder sample processed at 600°C for 30 minutes in a 100% O_2 atmosphere on a yttria stabilized zirconia substrate, the resulting grain morphology is indicative of grain growth from liquid phase sintering with grains seeming to spread out on the substrate.

XRD analysis on quenched samples indicates that for each composition in the series $\% \text{Cu} \leq 20\%$, multiple phases are present. Figures 3.7 and 3.8 show the experimental XRD data. Figure 3.7 compares the STO standard with the $\text{SrCu}_{0.03}\text{Ti}_{0.97}\text{O}_y$, $\text{SrCu}_{0.05}\text{Ti}_{0.95}\text{O}_y$, $\text{SrCu}_{0.075}\text{Ti}_{0.925}\text{O}_y$, and $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ bulk powder samples. Figure 3.8 compares the STO

Figure 3.5 Backscattered SEM image of $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ bulk powder pressed pellet heat treated at 1050°C for 180 hrs. in a 100% $\text{P}(\text{O}_2)$ atmosphere. For the 10% Cu doping level some evidence of liquid phase sintering is found within the resulting microstructure. The lighter regions in the figure outline the quenched in liquid phase.

Figure 3.6 Backscattered SEM image of $\text{SrCu}_{0.80}\text{Ti}_{0.20}\text{O}_x$ powder treated at 600°C for 30 minutes in a 100% $\text{P}(\text{O}_2)$ atmosphere. The microstructural features are indicative of a low melting temperature event that allowed for grain growth.

standard with the $\text{SrCu}_{0.13}\text{Ti}_{0.87}\text{O}_y$, $\text{SrCu}_{0.15}\text{Ti}_{0.85}\text{O}_y$, $\text{SrCu}_{0.17}\text{Ti}_{0.83}\text{O}_y$ and $\text{SrCu}_{0.20}\text{Ti}_{0.80}\text{O}_y$ bulk powder samples. STO diffraction peaks are identified with their respective reflections. Peaks that are denoted with an asterisk (*) correspond to reflections for the LaB_6 standard that was used for all XRD runs to confirm the accuracy of peak locations. A small amount of LaB_6 standard powder was mixed in with the powder sample prior to the data acquisition. Unmarked peaks correspond to the secondary phases that result from the addition of Cu to the STO structure.

According to experimental data, the primary phase for the Cu-doped bulk powders is STO at low Cu concentration levels. Additions of 3% Cu to the STO structure resulted in the formation of two additional secondary phases (revealed by SEM) and the substitution of Cu into the STO crystal structure (observed by TEM compositional analysis and XRD data refinement). The distinct phases were not discernable from the XRD data since their total percentage in the makeup of the Cu-doped compound was low. The presence of new peaks

Figure 3.7 XRD data collected for Cu-doped STO powders with $\%Cu \leq 10\%$. The data plots are presented in ascending order of $\%Cu$. The marked reflections correspond to the STO phase. Unmarked peaks represent the secondary phases resulting from the addition of Cu to the structure. The asterisk (*) denotes diffraction peaks for the LaB_6 standard used to verify peak locations. (a) STO, (b) $SrCu_{0.03}Ti_{0.97}O_y$, (c) $SrCu_{0.05}Ti_{0.95}O_y$, (d) $SrCu_{0.075}Ti_{0.925}O_y$, (e) $SrCu_{0.10}Ti_{0.90}O_y$.

Figure 3.8 XRD data collected for Cu-doped STO powders with $\%Cu < 20\%$. The data plots are presented in ascending order of $\%Cu$. The marked reflections correspond to the STO phase. Unmarked peaks represent the secondary phases resulting from the addition of Cu to the structure. The asterisk (*) denotes diffraction peaks for the LaB_6 standard used to verify peak locations. (a) STO, (b) $SrCu_{0.13}Ti_{0.87}O_y$, (c) $SrCu_{0.15}Ti_{0.85}O_y$, (d) $SrCu_{0.17}Ti_{0.83}O_y$, (e) $SrCu_{0.20}Ti_{0.80}O_y$.

in the XRD pattern indicated the existence of secondary phases that could not be identified due to the detection limits of the XRD technique. The process of searching and matching existing XRD powder diffraction card files for known compounds to the experimental data was not successful in identifying the new phases that formed. The number of secondary phases present was not apparent from the XRD data. This was the case for Cu additions $\leq 20\%$. As discussed earlier, SEM was used as a visual aid to distinguish the secondary phases. As will be addressed later, TEM compositional analysis techniques were used to determine approximate phase stoichiometries.

The Rietveld refinement method was employed to detect changes in the STO lattice parameter, which suggest Cu diffusion. The software chosen for this analysis was GSAS (General Structure Analysis Software) (8). GSAS is based on the Rietveld method that uses least squares refinement to fit an XRD experimental pattern to a calculated powder diffraction pattern (9). Several sample characteristics can be obtained from this method such as crystal structure and lattice parameters. The method was used to estimate lattice parameter values of the Cu-doped STO. Figure 3.9 shows the lattice parameter values for STO that were calculated for powder compositions in the range 0% Cu to 20% Cu. Only STO lattice parameters were calculated in order to observe the trend in lattice parameter change as the Cu percentage increased. Analysis of this data revealed that for the lower Cu composition samples ($\% \text{ Cu} \leq 20$), the Cu-doped STO lattice parameter was lower than that of the STO standard. The trend in the data showed the presence of the solubility limit of Cu in STO within this composition range. The drop in the lattice parameter between STO and the 1% Cu composition occurred due to the increased presence of secondary phases. The initial drop in lattice parameter value was observed at approximately 1% Cu. XRD analysis was implemented to determine the composition of the low melting temperature phase ($\sim 650^\circ\text{C}$) that was observed in the $\text{SrCu}_{0.80}\text{Ti}_{0.20}\text{O}_y$ bulk sample by SEM. According to XRD analysis, the low melting phase was $\text{Sr}(\text{NO}_3)_2$ (melting temperature= 570°C (6)).

Figure 3.10 provides a brief view of some of the microstructures as seen by TEM.

Figure 3.9 Lattice parameter evaluation of STO generated by refinement of experimental XRD data with GSAS. At 1% Cu compositions, the STO lattice parameter decreased.

Figure 3.10(a) shows the grain structure of $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ and 3.10(b) corresponds to that of $\text{SrCu}_{0.20}\text{Ti}_{0.90}\text{O}_y$. Although processed under identical conditions, the 10% Cu-doped powder resulted in a larger grain size in the sintered samples. By TEM EDS analysis, it was shown that Cu was substituting into the STO crystal structure, perhaps for Ti. According to the Cliff-Lorimer technique, the calculated compositions of the various phases within the bulk powder samples containing $\leq 20\%$ Cu are given in Figure 3.11. In each of the bulk samples the primary phase was $\text{Sr}_{0.51}\text{Ti}_{10.48}\text{O}_y$. This is the STO or $\text{Sr}_{1.02}\text{Cu}_{0.01}\text{Ti}_{0.96}\text{O}_y$ phase with 1% Cu substitution into the structure. While other phases may be present within the Cu-doped STO bulk powders according to XRD, the phase of particular interest was the one indicating that Cu had some solubility in STO for application to buffer layer design.

TEM EDS analysis of a sample prepared at the 50% doping level confirmed the presence of two distinct phases within the microstructure. Figure 3.12(a) shows that some Cu is present and identifiable in the STO matrix. In contrast, Figure 3.12(b) shows that the SrCuO_2 phase

Figure 3.10 TEM micrographs of (a) $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ and (b) $\text{SrCu}_{0.20}\text{Ti}_{0.90}\text{O}_y$ illustrating the difference in grain size with respect to similar processing conditions at varying Cu concentration levels.

Bulk Powder	$\text{Sr}_{0.51}\text{Cu}_{0.01}\text{Ti}_{0.48}\text{O}_x$	$\text{Sr}_{0.43}\text{Cu}_{0.21}\text{Ti}_{0.37}\text{O}_x$	$\text{Sr}_{0.21}\text{Cu}_{0.72}\text{Ti}_{0.07}\text{O}_x$	$\text{Sr}_{0.46}\text{Cu}_{0.28}\text{Ti}_{0.26}\text{O}_x$
$\text{SrCu}_{0.03}\text{Ti}_{0.97}\text{O}_x$	X		X	
$\text{SrCu}_{0.05}\text{Ti}_{0.95}\text{O}_x$	X			
$\text{SrCu}_{0.075}\text{Ti}_{0.925}\text{O}_x$	X			
$\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_x$	X	X	X	
$\text{SrCu}_{0.13}\text{Ti}_{0.87}\text{O}_x$	X			
$\text{SrCu}_{0.17}\text{Ti}_{0.83}\text{O}_x$	X			X
$\text{SrCu}_{0.20}\text{Ti}_{0.80}\text{O}_x$	X		X	X

Figure 3.11 Summary of phases identified by the Cliff-Lorimer method for Cu-doped STO samples.

is Ti free within the limits of the EDS system. This is an indication that Cu can diffuse into STO, but Ti does not substitute into SrCuO_2 . Based on the microstructural and compositional observations, a limited amount of Cu can substitute into the STO crystal structure. This is an important point to consider in the processing of YBCO coated conductors with STO buffer layers since interfacial reactions are a cause for degradation of the superconducting transport properties in these coated conductors (10). Addition of Cu to an STO buffer layer to the point of maximum solubility or saturation can minimize the loss of Cu suffered by

Figure 3.12 TEM EDS analysis of the $\text{SrCu}_{0.50}\text{Ti}_{0.50}\text{O}_x$ sample confirmed the presence of distinct phases within the structure (X denotes artifact peak). (a) EDS data shows that some Cu diffused into the STO phase. (b) The SrCuO_2 phase is apparently Ti-free, within the limits of the EDS system.

the YBCO.

3.4.4 SrO-CuO-TiO_2 Ternary Phase Diagram

Figure 3.13 outlines the regions of the SrO-CuO-TiO_2 ternary phase diagram at 1050°C in a 100% O_2 atmosphere that were determined by a combination of SEM, TEM, and XRD analysis techniques. The presence of a ternary phase was not identified within the regions analyzed. The phases are STO, Sr_2CuO_3 , SrCuO_2 , $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$, and CuO_2 . The $\text{Sr}_x\text{Cu}_y\text{O}_z$ phases do not accommodate Ti. The Cu-doped STO phase that forms is negligible when compared to the other phases and cannot be characterized by XRD.

3.5 DISCUSSION

SEM, TEM, and XRD characterization techniques were applied to establish phase evolution and solubility limits of Cu in STO. The heat treatment atmosphere was found to affect the resulting secondary phase distribution. At 100% $\text{P}(\text{O}_2)$ atmosphere, secondary phases formed as large conglomerations when compared to the distribution of these phases at low $\text{P}(\text{O}_2)$, as shown in Figure 3.3. Low $\text{P}(\text{O}_2)$ thermal processing atmospheres were more conducive to the formation of uniform microstructures in bulk samples. Regardless

Figure 3.13 Phase diagram schematic for the SrO-CuO-TiO₂ ternary system. A ternary phase was not identified within the regions analyzed.

of sample uniformity, the addition of Cu to the STO structure increased porosity. This was observed at Cu additions as low as 1%. Bulk powder samples were prepared by dissolving SrCO₃, CuO, and TiO₂ in nitric acid to dissolve the carbonates. Thermal processing of the bulk powder was carried out to remove remaining nitrates after drying the powder in vacuum conditions. XRD results indicated that the thermal processing conditions were inadequate for complete removal of nitrates. Even though the processing conditions were not optimum for nitrate removal, the Sr(NO₃)₂ phase can be beneficial to reducing the porosity introduced by the Cu additions to STO. Thermal processing of the powders at temperatures higher than the Sr(NO₃)₂ melting temperature allow for melting and dispersion of the Sr(NO₃)₂ phase throughout the microstructure. The Sr(NO₃)₂ phase may have responsible for the liquid phase sintering that was observed to densify the microstructure. This behavior was predominant in the 10 % Cu and the 20% Cu doping level as seen in Figure 3.4 (e) and (i). As a result of

bulk powder processing conditions, the concentration of $\text{Sr}(\text{NO}_3)_2$ was more pronounced at these doping levels as shown by a secondary phase that connects neighboring pores. Higher levels of $\text{Sr}(\text{NO}_3)_2$ in the Cu-doped STO matrix can promote increased densification that will yield smooth, dense buffer layers. This poses an interesting result that is worthy of future investigation because $\text{Sr}(\text{NO}_3)_2$ can be incorporated into the chemistry of the buffer layer to compensate for resulting porosity if the presence of this phase does not hinder YBCO superconducting capability. The compatibility of the Cu-doped STO buffer layer and YBCO is addressed in the following chapter.

TEM EDS compositional analysis and XRD analysis indicated that the solubility limit of Cu in STO was $\sim 1\%$. Based on measured compositions by x-ray microanalysis, Cu appeared to substitute for the Ti into the STO structure due to the respective ionic radii of $0.87 \text{ \AA}$ for Cu and $1.00 \text{ \AA}$ for Ti. Ti did not substitute into the SrCuO_2 structure as shown by the x-ray spectra in Figure 3.12. XRD spectra of bulk powders with Cu compositions less than 20% showed the presence of diffraction peaks corresponding to secondary phases. The unidentified diffraction peaks may correspond to the $\text{Sr}_{0.51}\text{Cu}_{0.01}\text{Ti}_{0.48}\text{O}_y$ phase that was identified by the Cliff-Lorimer technique. The percentage of this phase in the total composition of the bulk powders is negligible when compared to the STO and SrCuO phases that were identified.

3.6 SUMMARY

XRD, SEM, and TEM analysis showed that the solubility of Cu in STO was $\sim 1\%$. Processing atmospheres were found to affect secondary phase distribution in the bulk powders. XRD analysis of the bulk powders showed that $\text{Sr}(\text{NO}_3)_2$ was present in the powders. This lower melting temperature phase may have contributed to the liquid phase sintering observed in the bulk powders, specifically in the 10% and 20% Cu-doped STO. A ternary phase was not identified in the regions of the ternary system that were studied. The confirmed phases were STO and SrCuO_2 .

3.7 REFERENCES

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YBa₂Cu₃O_{7-δ} COATED CONDUCTOR STRUCTURE WITH SrCu_{0.01}Ti_{0.90}O_y BUFFER LAYER BY PULSED LASER DEPOSITION

*The human mind prefers to be spoon-fed
with the thoughts of others, but deprived of such
nourishment it will, reluctantly, begin to think for itself—
and such thinking, remember, is original thinking
and may have valuable results.*

— Agatha Christie (1890–1976)
English author, dramatist. Her play
“Mousetrap” is the longest running in British history.

- 4.1 ABSTRACT
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4.1 ABSTRACT

The microstructural evolution of epitaxial YBa₂Cu₃O_{7-δ} (YBCO) coated conductors fabricated by pulsed laser deposition (PLD) on (100) SrCu_{0.10}Ti_{0.90}O_y buffered (100) magnesium oxide (MgO) substrate was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Copper (Cu) was added to the SrTiO₃ (STO) buffer layer to address concerns of Cu migration and depletion in the YBCO film. The resulting coated conductor structure consisted of a 100 nm thick SrCu_{0.10}Ti_{0.90}O_x film and a 600 nm thick YBCO film with an in-plane texture spread of 6.5°. The corresponding superconducting properties were: critical temperature (T_c) = 87 K and critical current density (J_c) = 1 MA/cm². SEM analysis of the YBCO thin film showed that the surface was characterized by voids as well as misaligned grains protruding from the film. TEM analysis revealed the formation of interfacial reaction products and misalignment of the YBCO grains. The results of this work will be submitted for publication. The research collaborators were T.G. Holesinger and Q.X. Jia.

4.2 INTRODUCTION

$\text{YBa}_2\text{Cu}_3\text{O}_{7-8}$ (YBCO) coated conductors are thin film structures consisting of a series of buffer layers that increase the compatibility of the substrate material and the YBCO superconducting layer. The buffer layer or layers must enhance structural compatibility, thermal stability, and chemical stability with the YBCO and the underlying substrate. Since the 1987 discovery of the YBCO superconductor, the buffer layer that yields the highest critical current (I_c) and critical current density (J_c) has evolved from ion beam assisted deposition (IBAD) yttria stabilized zirconia (YSZ) to IBAD magnesium oxide (MgO) because the deposition time of the latter is 0.01 of that required by YSZ for similar superconducting properties (1, 2). The detrimental features of the direct combination of YBCO and MgO are that the lattice mismatch between the two is 9% and the hygroscopic nature of the MgO hinders thin film reproducibility (3, 4). Due to the high lattice mismatch, films grown on MgO exhibit a lower critical temperature (T_c) and I_c , by as much as a factor of 10 (4), than those deposited on perovskite substrates such as SrTiO_3 (STO) (4, 5). The reactive nature of the YBCO poses a challenge in finding an adhering buffer layer that is accepted by the YBCO and the substrate material. High performance YBCO films with critical current densities over 1 MA/cm^2 have been grown on lanthanum manganate (LaMnO_3) (4), strontium ruthenate (SrRuO_3) (5), and STO buffer layers (6-9). The focus of this research is to introduce copper (Cu) into the STO buffer layer of the YBCO coated conductor structure to investigate interfacial compatibility as well as effects on superconducting capability (10). The current chapter documents the microstructural behavior of the YBCO coated conductor with a $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ buffer layer.

4.3 EXPERIMENTAL TECHNIQUE

Coated conductors are fabricated in a series of steps involving IBAD and pulsed laser deposition (PLD) processes. IBAD was used to grow a biaxially textured MgO layer and a homoepitaxial MgO layer on a 100 μm thick, 1 cm wide commercial Hastelloy C276

strip. The surface roughness of the substrate was 2-4 nm, achieved by mechanical polishing. Prior to loading into the deposition chamber the tapes were rinsed and vacuum annealed at 800°C and 10^{-6} torr to remove any oxide films that may have been present on the surface. Once in the deposition chamber, the metal substrate was ion etched prior to the actual MgO deposition. The IBAD MgO was then deposited onto moving, meter-long lengths of the Hastelloy maintained at room temperature. Following the deposition of the IBAD MgO, the meter long tape was sectioned in preparation for PLD deposition.

The $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ and YBCO films were deposited by PLD with a XeCl excimer laser (Lambda Physik $\lambda = 308$ nm, 10 Hz) in a separate chamber at a temperature of 760°C and an O_2 pressure of 200 mTorr. For PLD deposition of $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ a 0.25" thick, 3" diameter target was pressed from the processed powder. Bulk powder preparation technique for the $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ compound is described in Chapter 3. 1 cm x 1 cm substrates were affixed with silver paste to a substrate holder block maintained at a temperature of 760°C throughout the deposition process. The $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ was grown to a total thickness of ~ 0.099 μm while the thickness of the YBCO layer was ~ 0.60 μm . The final deposition in the sequence of layers was a ~ 1 μm thick silver (Ag) layer. The Ag film was sputtered at room temperature and served the purpose of shielding the YBCO layer from the environment as well as providing an electrical contact to the superconducting film. An external furnace anneal at 300°C in flowing oxygen for 30 minutes followed by furnace cooling to room temperature ensured proper oxygenation and bonding of the Ag to the YBCO film.

The coated conductor was characterized for superconducting properties and structural features. T_c and I_c were measured at liquid nitrogen temperature in self-field over the entire 1 cm width. A Siemens diffractometer was used to determine average in-plane and out-of-plane film texture using $\text{CuK}_{\alpha 1}$ radiation for θ -2 θ . Scanning electron microscopy (SEM) analysis was performed with a JEOL 3000 SEM. A Philips CM transmission electron microscope was used for transmission electron microscopy (TEM) analysis. TEM and SEM samples were prepared for viewing in the longitudinal transverse direction (perpendicular to both

the nominal c axis of the film and the direction of current flow). Cross-sectional specimens were prepared by cutting the samples and gluing two thin film slices film to film between two slices of silicon. The samples were then placed inside 3 mm nonmagnetic stainless steel tubes using torr seal™ to seal the samples into the tube. The stainless steel tube was sliced into ~220 µm thick slices. The thin discs were then ground on both sides with silicon carbide grits sizes 400-1200 to a thickness of ~110 µm followed by dimple polishing on both sides with 3 µm, 1 µm, and 0.25 µm diamond paste using a 0.10 µm diamond slurry for the lubricant. The discs were thinned to electron transparency by ion beam milling on a Gatan ion mill. The duration of the ion milling was approximately 3 hours at a voltage of 3.5 kV at an angle of 4° with respect to the surface of the disc.

4.4 RESULTS AND DISCUSSION

4.4.1 YBCO Coated Conductor In-Plane Texture

According to structural analysis by XRD the texture of the IBAD MgO template was ~13°. At this point it is significant to note that since the fabrication of the IBAD MgO tapes used in this research, considerable improvements in texture have been achieved. The texture of the IBAD MgO has evolved from ~11° (11) to ~5.1-5.5° (12) by reducing the starting metal substrate roughness to < 1 nm RMS (atomic force microscopy, 5 x 5 µm scan area) and by optimizing ion beam deposition parameters. At the time of this research, an IBAD MgO template with a texture of ~13° was the best that could be obtained to meet the proposed objectives.

The measured in-plane texture for the YBCO superconducting film was ~6.5°. The improvement in texture from ~13° for the IBAD MgO to ~6.5° for the YBCO is noteworthy. The introduction of a $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ buffer layer to the YBCO coated conductor structure seems to have been beneficial in terms of enhancing the alignment of the YBCO growth

template. Optimization of the modified STO buffer layer calls for reduction of the YBCO in-plane texture spread. Although, it has been shown that YBCO texture is not the only variable that must be considered in the design of the YBCO coated conductor architecture (6).

4.4.2 $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ and YBCO Surface Morphology

SEM was used to evaluate the surface morphology of the $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ film as well as that of the YBCO film. Figure 4.1 shows an SEM view of the surface of the $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ film deposited on the (100) IBAD MgO. Spherical droplets less than $0.1\text{ }\mu\text{m}$ in diameter are a characteristic feature of the surface morphology. The upper region of the micrograph also reveals the presence of a void ($< 0.1\text{ }\mu\text{m}$ in diameter) on the surface of the film. Aside from the recurring droplets, the $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ film has a relatively smooth surface. There are two possible explanations for the presence of the spherical droplets. The spherical droplets may be attributed to the particulate deposition problem associated with the PLD technique (3, 13-16). By-products of the PLD process result from the expulsion of particles from the

Figure 4.1 SEM microstructural view of the surface of the $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ film deposited by PLD on IBAD MgO. The spherical droplets are most likely the byproduct of the particulate deposition problem associated with PLD.

target due to the violent laser/target interaction during the deposition process. Spheres are a telltale sign of the particle problem because there exists a critical particle size that establishes the limits of survival of particles on the surface. Particles that are smaller than the critical size will “melt” by absorption of energy through their surfaces (16). The extent of the particulate deposition problem can be assessed by the density of spheres on the surface of the film.

Another possible explanation for the nature of the spherical particles on the surface of the $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ film is the outgrowth formation model proposed by Cheng, et al. (16). According to this model, the spherical droplets characteristic of the film morphology would be referred to as outgrowths rather than particulates. The origin of these outgrowths rests in the film nucleation and growth process. If the deposition parameters of temperature and deposition rate are optimized, then there is one unique film thickness that allows for complete nuclei coalescence and avoids the formation of outgrowths resulting in the lowest achievable surface roughness. The film thickness required for complete coalescence seems to depend on PLD deposition rates. Faster deposition rates tend to yield complete film coalescence at smaller thicknesses.

Based on the ramifications of the two possible causes of the surface morphology illustrated in Figure 4.1, it may be concluded that the spherical droplets are a direct result of the particulate deposition problem. The spheres are evenly distributed on the surface and it is speculated that outgrowths could not occur with such periodicity. The smooth appearance of the film indicates complete coalescence at the chosen deposition conditions.

Figure 4.2 shows the granular structure of the YBCO film (0.25 μm grain size) deposited by PLD on the $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ buffer layer. Similar to the buffer layer surface, the YBCO surface has spherical droplets, although these are not the prominent feature. Thus, the degree of particulate deposition is not as extensive as in the case of the buffer layer. Other significant irregularities in the YBCO film are needle-like outgrowths and voids within the grains. The voids are evenly distributed throughout the film and are most likely the result of incomplete film coalescence. Overall, these voids produce the appearance of unconnected grains.

Figure 4.2 SEM micrograph showing the surface of the YBCO film deposited by PLD on the $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ buffer layer. The surface irregularities on the film can be classified as spherical droplets, voids, and outgrowths. The inset in (a) shows a schematic of a-axis grain growth. The a planes are perpendicular to the horizontal c planes of the surrounding YBCO film.

The needle-like outgrowths on the surface of the film are grains that have transitioned from thermodynamically preferred growth to kinetically preferred growth (17). YBCO films grown at elevated temperatures ($\sim 800^{\circ}\text{C}$) tend to be c-axis films, i.e., the direction of growth is along the c-axis normal to the surface of the substrate (18). On the other hand, lower growth temperatures ($\sim 650^{\circ}\text{C}$) yield a-axis films, i.e., the direction of growth is along the a-axis normal to the substrate surface (18). A-axis oriented grains have c planes that are perpendicular to the horizontal c planes of the c-axis grains. Optimal superconducting properties are observed on c-axis films, however, traces of a-axis oriented growth may still be present in these films. C-axis growth is the preferred growth mode of YBCO according to thermodynamics because throughout the process it yields the lowest energy crystal termination. The grain growth occurs parallel to the surface of the film, thus significant quantities of surface diffusion are required to grow a layer one unit cell in thickness. Kinetics dictates a change in crystal orientation to a-axis growth, growth normal to the film surface, because it eliminates the need for surface diffusion since the grains are growing normal to the film surface, the active growth sites receive the incoming flux. Due to their direction of growth, a-axis grains become outgrowths on the surface of the film (19). The thermodynamically preferred c-axis grains dominate the final YBCO microstructure because once the YBCO film covers the entire substrate surface, the c-axis grains grow over the a-axis oriented grains (20).

4.4.3 YBCO coated conductor cross-section

Figures 4.3-4.6 depict the overall microstructure of the $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ buffer layer and the subsequent YBCO coated conductor based on this buffer layer. Figure 4.3 shows a cross-sectional view of the $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ buffer layer deposited by PLD onto the IBAD MgO. The $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ film is characterized by (100) directional growth and exhibits a grain size of ~ 50 nm. The absence of obvious secondary reaction products along the MgO/ $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ interface implies some degree of compatibility between the two buffer

Figure 4.3 TEM micrograph of the $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ buffer layer deposited on IBAD MgO by PLD.

layer materials. This is desirable in setting up the foundation for the YBCO film since previous research has shown that optimum superconducting properties can be obtained through the use of two buffer layers (21). The first buffer layer provides the biaxially textured template required for oriented growth of subsequent layers (21) and prevents diffusion between the metallic substrate and the YBCO film (23). The second buffer layer improves the lattice mismatch between the YBCO (24) and the first buffer layer while diminishing the reactivity of the YBCO (25). The lattice mismatch between MgO and YBCO is 9.67% while that between STO and YBCO is 1.5 % (26). Thus, an STO buffer layer in the coated conductor architecture improves the alignment of the YBCO film.

Figures 4.4-4.6 address the microstructural features arising from the deposition of a 600 nm thick YBCO film on the $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ buffer layer. The corresponding J_c value for

Figure 4.4 TEM composite micrograph of the YBCO coated conductor with the $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ buffer layer. The white arrows denote the occurrence of unfavorable reaction products along MgO/substrate boundary.

Figure 4.5 TEM mapping of the YBCO coated conductor illustrating interfacial reaction products along the MgO/substrate boundary (white arrows) and YBCO misalignment on interfacial reaction phases (black arrows).

Figure 4.6 TEM microstructural views of select regions of the $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ based YBCO coated conductor. The appropriate layer sequence is identified in (a). The regions depicted in (a), (b), and (c) show that the proximity of $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ and YBCO result in the formation of interfacial reaction products that are comparable in size to the total thickness of the $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ layer. The interfacial products affect the alignment of the YBCO film.

this coated conductor was 0.75 MA/cm² at 87 K and self-field. Similar to results of other research efforts (21, 27), the in-plane texture of the structure improved with each successive film deposition process. The starting texture of the IBAD MgO was 13°, in comparison to a final YBCO texture of 6.5°.

The section of the YBCO film shown in Figure 4.4 indicates the presence of secondary reaction products along the substrate interface. These secondary reaction products were absent prior to the deposition of the YBCO film as revealed in Figure 4.3. In order to minimize or eliminate interfacial reaction products, the substrate of choice for coated conductors is typically nickel or a nickel-based alloy due to their oxidation resistance at the high temperature required to deposit YBCO by PLD (21). For the coated conductor based on the SrCu_{0.10}Ti_{0.90}O_y buffer layer, it appears that the nickel-based substrate was not immune to secondary reactions.

Analysis of Figure 4.4 indicates that the YBCO film is dense and continuous throughout; however, Figures 4.5 and 4.6 reveal a different nature. The white arrows in Figure 4.6 point to interfacial reactions along the MgO/substrate boundary that occurred during the deposition of the YBCO, as comparison of Figures 4.3 and 4.4 indicate. The black arrows identify areas of the film where YBCO is misaligned in areas adjacent to interfacial reaction phases. The series of TEM micrographs in Figure 4.6 show that the products of interfacial reactions are comparable in size to the total thickness of the SrCu_{0.10}Ti_{0.90}O_y layer. Optimization of the coated conductor structure and the corresponding superconducting properties requires uninterrupted through-structure alignment. The presence of interfacial reactions may be attributed to limited compatibility between the YBCO and SrCu_{0.10}Ti_{0.90}O_y or perhaps to inadequate deposition conditions for the particular material system.

4.5 SUMMARY

The YBCO coated conductor based on a SrCu_{0.10}Ti_{0.90}O_y buffer layer exhibits microstructural defects that may hinder its superconducting performance. The products

of interfacial reactions affected the alignment of the YBCO along the $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ boundary. The size of secondary products was observed to exceed the the total thickness of the $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ film. Although, the in-plane texture spread did improve with successive layer deposition, unfavorable microstructural interactions did not permit attainment of J_c values similar to those of high performance YBCO coated conductors.

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THE DEPOSITION OF SINGLE-LAYER EPITAXIAL SrTiO_3 AND COPPER-DOPED SrTiO_3 FILMS ON ION BEAM ASSISTED DEPOSITION MAGNESIUM OXIDE TEMPLATES BY CHEMICAL SOLUTION DEPOSITION

*Who were the fools who spread the story that brute force
cannot kill ideas? Nothing is easier. And once they
are dead they are no more than corpses.*

— Simone Weil (1909–1943)

French philosopher, activist. She was a mystic
and an activist in the French Resistance during WW II.

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5.1 ABSTRACT

Epitaxial SrTiO_3 (STO) and Cu-substituted STO buffer layers were processed by the chelate method approach to chemical solution deposition (CSD) on ion-beam-assisted deposition (IBAD) magnesium oxide (MgO) flexible metallic textured tapes. The STO thin films were deposited by spin coating and heat treated in a low oxygen partial pressure ($\text{P}(\text{O}_2)$) atmosphere in a two-step process. Transmission electron microscopy (TEM) analysis showed average film thickness of 30 nm and columnar film growth initiated by heterogeneous nucleation. X-ray diffraction (XRD) analysis revealed an in-plane texture of $\sim 11^\circ$ on an IBAD MgO substrate with $\sim 13^\circ$ in-plane texture. A layer of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) was deposited onto the STO and copper (Cu) doped STO buffer layers by pulsed laser deposition (PLD). Preferred orientation was found to transfer through the series of layers of the thin film composite. The measured critical temperature (T_c) of the YBCO coated conductor fabricated

by a combination of CSD and PLD was ~ 80 K. The results of this work will be submitted for publication. The research collaborators were T.G. Holesinger, P.G. Clem, V. Matias, H. Wang, B. Gibbons, and R.F. DePaula, and R. Groves.

5.2 INTRODUCTION

Broad-scale commercialization of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) superconductors is suffering a setback due to the high costs associated with production. Conventionally, *in situ* deposition methods such as sputtering, laser ablation, pulsed laser deposition (PLD), and ion beam assisted deposition (IBAD) are used to prepare the series of layers comprising the coated conductor structure. While producing promising results, the costs involved in carrying out the actual deposition process and maintaining the equipment keep the price performance of the YBCO superconductor above the $\$10 \text{ kA m}^{-1}$ limit (1, 2). Strides in large-scale production of YBCO coated conductors will be achieved if scientific and engineering research goals focus on high rate deposition of quality thin films.

Perovskite oxide thin films are proving to be indispensable in applications such as capacitors, magnets, motors, electro-optic devices, electroluminescent displays, and superconductors (3, 4). The use of chemical solution deposition (CSD) techniques to deposit perovskite thin films is gaining widespread attention due to its potential economic impact on production costs. Featuring the use of simple equipment that does not require a vacuum environment, CSD promises high production rates at a fraction of the cost of other deposition means such as PLD and IBAD. Successful deposition of perovskite thin films by CSD depends on optimization of process parameters to yield high-quality films. In regards to thin films, high-quality refers to film homogeneity, accurate film stoichiometry, absence of cracks, low surface roughness, and film texture approaching that of a single crystal, $\sim 1^\circ$.

Film texture is important for superconductors to carry maximum current density, (J_c). The intergrain J_c decreases by approximately two orders of magnitude relative to the intragrain J_c if the misorientation angle is $> 20^\circ$, however J_c increases exponentially as the misorientation

angle decreases (5). Studies have shown that at misorientation angles of 4° - 7° , the intergrain and intragrain J_c values are equivalent (6). This behavior has been attributed to the nature of small angle grain boundaries (7). These boundaries are made up of dislocation islands separated by channels of perfect crystallinity that are wide when compared to the size of the dislocations. In this case, the intergrain and intragrain J_c are essentially equivalent because the area occupied by the crystalline channels overshadows that of the isolated dislocations to the point where their effect on the grain boundary area is negligible. Recent progress in IBAD MgO buffer layer deposition has led to textures well within the 4° - 7° range that yielded acceptable J_c values ($J_c > 1 \text{ MA/cm}^2$) (5).

Deposition kinetics and microstructural evolution must be understood in order to tailor deposition conditions and to develop a controllable fabrication scheme. From beginning to end, every step of the CSD process (similar to other deposition process e.g.) can affect the resulting thin film structure. Important variables in the CSD process include, but are not limited to: starting reagents for the precursor solution; precursor solution molarity and shelf life; thin film/substrate compatibility; and deposition conditions such as speed and duration, subsequent heat treatment temperatures, time, and atmospheres. Previous research has shown that modifications in precursor chemistries can affect grain size and orientation of the perovskite thin films (8-11). The extent of contact between the precursor solution and substrate, determined by features such as surface roughness and lattice matching, also affect the final film microstructure (12). Once the substrate and precursor chemistry have been selected, subsequent processing conditions must be evaluated to maintain the structural integrity of the thin film. Heat treating for crystallization must be conducted under controlled conditions as variations in annealing temperature affect the film microstructure (8, 13).

The goal of this portion of the research was to apply CSD technology to develop high-quality, epitaxial, STO thin films on IBAD MgO coated conductor substrates. Epitaxy refers to the growth of a film of one material onto another material where the periodicity of atoms on the surface of the substrate is the template for the growth of the thin film, i.e.

epitaxial growth. The STO thin films were epitaxial on the underlying IBAD MgO without requiring the use of an STO nucleating seed layer. Previously, epitaxial STO thin films have been grown only on single crystal substrates or by the use of an intervening seed layer that provides preferentially oriented nucleation sites for the STO (14-20).

5.3 EXPERIMENTAL PROCEDURE

5.3.1 Precursor Solution Synthesis

Figure 5.1 outlines the preparation route for precursor solutions and thin films. The STO precursor solution was prepared by dissolving a given amount of reagent grade strontium acetate ($\text{Sr}(\text{OOCCH}_3)_2$, Alfa Aesar) in glacial acetic acid at a temperature of 90°C under continuous stirring at 300 rpm on a hot plate for 1 hour. Once the strontium acetate dissolved in the glacial acetic acid, the solution was cooled to room temperature and the appropriate amounts of reagent grade titanium isopropoxide ($\text{Ti}(\text{OCH}(\text{CH}_3)_2)_4$, Alfa Aesar) and anhydrous methanol were added to the solution. Copper acetate ($\text{C}_4\text{H}_6\text{CuO}_4$, Alfa Aesar) was added prior to the titanium isopropoxide for Cu-doped STO thin films. The solutions were prepared in a fume hood 2 hours prior to the spin coating operation and were promptly discarded after deposition to avoid effects produced by aging solutions which is a side effect of the chelate processing method.

5.3.2 Thin Film Synthesis

The substrate of choice for the STO thin films was a Ni-alloy tape coated with one layer of Al_2O_3 followed by a layer of (100) IBAD MgO and a layer of (100) homoepitaxial MgO. Thus, the thin film deposition was directly onto the (100) homoepitaxial MgO. The substrates were received in long lengths, up to 50 cm, from the coated conductor fabrication team at Los Alamos National Laboratory. For spin coating, the substrate tape was sectioned into 1 cm x 1 cm samples. Substrate cleaning with any chemical prior to spin

Solution Synthesis

Figure 5.1. Summary of experimental route for the preparation of STO thin films by chemical solution deposition.

coating was avoided to prevent structural damage to the surface of the (100) homoepitaxial MgO. Ultra-high purity nitrogen was used to blow off any particles resting on the surface of the substrates before spin coating. Spin coating was carried out using a Chemat Spin Coater Model KW-4A. The substrates were held on the spin coater by a vacuum. The precursor solution was dispensed onto the surface of the substrate by a filtered syringe (0.2 mm Teflon filter) and spin coated at 3000 rpm for 30 seconds in a fume hood. The as-coated thin films were thermally processed in a two stage process. The thin films were pyrolyzed at 200°C for 20 minutes in a 10% P(O₂) atmosphere (balance Ar) in an Al₂O₃ tube furnace. The ramp rates for the heating and cooling stages were set at 1°C /min. to allow the newly deposited thin film to dry at a controlled rate to prevent mud cracks. The crystallization heat treatment was carried out in the same tube furnace in a 1% P(O₂) (balance Ar) atmosphere at a temperature of 850°C for 1 hour. The ramp rate for the crystallization treatment was: 5°C/min. to 400°C, 10°C/min. to 850°C, 3°C/min. to 400°C, 5°C/min. to 25°C. X-ray diffraction (XRD) was used to determine film composition as well as in-plane and out-of-plane texture. Reflection high energy electron diffraction (RHEED) analysis was used to optimize crystallization temperature and dwell times. Thin film surface characteristics were determined by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Transmission electron microscopy (TEM) was used to evaluate the thin film microstructure and interfacial interactions along neighboring layers.

5.4 RESULTS

5.4.1 Precursor Solution Concentration

Precursor solution concentrations ranged from 0.1 M to 0.45 M in the initial stages of the research in order to determine the optimum solution molarity for the STO thin films. A molarity of 0.45 was found to exceed the solubility limit of the mixture. This precursor solution was cloudy and contained precipitates which produced uneven, rough films.

A molarity of 0.3 seems to be the upper limit for the STO solution. Figure 5.2 shows a series of SEM micrographs corresponding to STO thin films derived from precursor solutions of different molarities. For the reported results, the molarity of the precursor solution is 0.2 M.

5.4.2 Thin Film Pyrolysis

Prior to the crystallization anneal, the as-deposited film undergoes a thermal treatment at temperatures ranging from 200-400°C to burn out the organic species. Typically, as-deposited thin films are pyrolyzed on a hot plate. Even though the films are thermally shocked by this process, it is the best approach with few if any cracking problems being reported (20). Research suggests that the amorphous thin film network does not crack in the intermediate pyrolysis step which eliminates organic film components. Lakeman et al., have studied the structural rearrangements that occur during pyrolysis (21). Their research findings indicated that as-deposited amorphous films were characterized by short-range order while as-pyrolyzed films possessed medium-range order.

Contrary to reports in literature documenting the absence of cracks following pyrolysis on a hot plate, preliminary SEM analysis of STO thin films on IBAD MgO revealed cracks throughout the film microstructure. Crack formation appears to have initiated during pyrolysis and progressed during subsequent heat treatment. Therefore, rather than thermally shocking the samples by carrying out pyrolysis at a high rate of cooling on a hot plate exposed to ambient laboratory conditions, thin film pyrolysis was conducted in an alumina tube furnace under a controlled atmosphere. A series of STO thin films were subjected to pyrolysis treatments at 1% P(O₂) and 10 % P(O₂) (with an Ar balance) dry and humid atmospheres to investigate the effects of varying P(O₂) and humidity on the surface morphology. Humid atmospheres, generally helium saturated with water vapor, are only required in the processing of solution deposited YBCO thin films to form the superconducting phase (22). It was of interest to study the effects of humidity on the crystallization of the STO thin films. The thin

Figure 5.2 SEM micrographs showing the surface morphology of STO thin films deposited from precursor solutions of different molarities. (a) 0.05 M STO, (b) 0.15 M STO, (c) 0.2 M STO, (d) 0.3 M STO.

films were deposited, pyrolyzed at 200°C for 20 minutes in a 1% and 10% P(O₂) dry and humid atmosphere, and processed at either 750°C or 850°C for crystallization. The humid atmosphere was obtained by feeding a stream of either 1% or 10% P(O₂) through a water bath maintained at 70°C.

Figure 5.3 shows an SEM comparison of the effects of pyrolysis atmosphere on the surface morphology of thin films thermally processed at 750°C. At 750°C at both 1% and 10% P(O₂), the humid atmosphere produces an island-type thin film morphology. The islands are more

pronounced at 10% P(O₂). AFM analysis of the films yielded roughness values of 90 and 150 Å for the films treated at 1% and 10% P(O₂), respectively. For both P(O₂) conditions in a dry atmosphere, the thin films were uniform and continuous. The roughness values of the films were 15 and 10 Å for the 1% and 10% P(O₂) conditions, respectively.

Similar results were obtained for the 0.2 M STO thin films processed at 850°C for crystallization as shown in Figure 5.4. The exception was the thin film pyrolyzed in a 1% P(O₂) dry atmosphere that crystallized into an island-type formation. The corresponding surface roughness values for this set of samples were 50, 12, 100, and 185 Å for the 1% (PO₂) dry, 10% P(O₂) dry, 1% P(O₂) humid, and 10% P(O₂) humid pyrolysis conditions. Based on these observations, the pyrolysis atmosphere was maintained at 10% P(O₂) under dry conditions.

5.4.3 Thin Film Crystallization Theory: Gel to Ceramic Transformation

Following the spin coating operation, the thin films are amorphous. Transformation of the amorphous thin film to a crystallized film depends on factors such as thin film-substrate interactions, solution chemistry, transformation pathway, and thermal processing conditions. It is imperative that the amorphous to crystalline conversion avoid the formation of residual intermediate phases in the final crystallized film. Such intermediate phases must be avoided to preserve film quality and performance (20). Similar to previous research (3, 23, 24), the STO thin films produced in this study were single phase according to XRD analysis as shown in Figure 5.5. The sharp diffraction peak at a 2θ value of ~43° shown in the XRD data plot in Figure 5.5 corresponds to the Ni-alloy substrate and the homoepitaxial MgO layer. At this particular 2θ value, the MgO and Ni diffraction peaks overlap. The smaller, less pronounced peak at a 2θ value of ~46° corresponds to the (200) diffraction peak of STO. The thickness of the STO thin film used for this analysis was only ~30 nm and for this reason the thicker Ni substrate and MgO layer yield diffraction peaks that overshadow the STO peak. Diffraction analysis of the thin film reveals only peaks for the Ni substrate, the MgO layer, and the STO

Figure 5.3 SEM micrographs of 0.2 M STO thin films pyrolyzed at 200°C for 20 minutes in dry and humid atmospheres and processed for crystallization at 750°C. (a) 1% O₂ dry, (b) 10% O₂ dry, (c) 1% O₂ humid, (d) 10% O₂ humid.

Figure 5.4 SEM micrographs of 0.2 M STO thin films pyrolyzed at 200°C for 20 minutes in dry and humid atmospheres and processed for crystallization at 850°C. (a) 1% O₂ dry, (b) 10% O₂ dry, (c) 1% O₂ humid, (d) 10% O₂ humid.

thin film. The STO thin film grown by CSD is single phase.

The next step in processing the single phase STO thin films was to optimize thin film processing conditions to obtain crystalline, epitaxially oriented thin films. Thin film crystallization must be controlled to optimize thin film quality and reproducibility. The first step to thermal processing of the STO thin films was to identify the temperature of crystallization. Reflection high energy electron diffraction (RHEED) was employed for this purpose. The samples were maintained in a low $P(O_2)$ vacuum atmosphere for the duration of the analysis and were heated to temperature at a rate of $1^\circ\text{C}/\text{min}$. Figure 5.6 shows a sequence of RHEED patterns for 0.2 M STO thin films. The first RHEED pattern corresponds to an as-pyrolyzed STO thin film that is ready for the crystallization treatment. The RHEED pattern confirms the amorphous state of the film. The subsequent three patterns illustrate the evolution of the thin film microstructure as the processing temperature increases. At 740°C (Figure 5.6(b)), the film remained in the amorphous state as indicated by the absence of reflection spots. At 750°C , the RHEED pattern showed a faint polycrystalline ring formation,

Figure 5.5 XRD data plot of a ~ 30 nm STO thin film deposited on IBAD MgO by CSD. The diffraction peak at $\sim 43^\circ$ corresponds to overlapping reflections of the Ni substrate and MgO layer. The peak at $\sim 46^\circ$ denotes the (200) STO diffraction. The presence of only the Ni, MgO and STO peaks indicates that the thin film deposited by CSD is single phase.

indicating the start of the amorphous to crystalline transition. This is in contrast to previous reports documenting that STO thin films crystallize at temperatures as low as 450°C in air atmospheres (3, 4). At 760° the polycrystalline rings are more well-defined. According to this RHEED sequence, the lower limit for the crystallization temperature of the 0.2 M STO thin films is ~750°C. Also, the series of RHEED patterns collected during heating to the anneal temperature showed that nucleation and grain growth started during the ramp up to the anneal temperature.

Identification of the critical crystallization temperature of the STO thin films established

Figure 5.6 In-situ RHEED images captured at varying temperatures to determine the temperature of crystallization for the 0.2 M STO thin films. The thin films were only pyrolyzed, as described in the experimental technique, prior to the RHEED analysis. Thermal processing for crystallization was performed in the RHEED chamber to monitor the evolution from an amorphous to crystalline microstructure. (a) as spin-coated amorphous film, (b) 740°C, (c) 750°C, (d) 760°C.

only the lower limit of the temperature range for thermal processing. Other processing parameters that warranted quantification were: (a) the processing temperature that optimized thin film structure; and (b) the dwell or soak time required at high temperature. The definition of an optimized thin film structure is research-specific. In this case, the film must follow the (100) orientation of the MgO layer, i.e., epitaxial growth. RHEED was again used to define processing parameters, keeping in mind that it can only assess whether a film is predominantly oriented in one direction in a qualitative sense. Figure 5.7 shows a sequence of RHEED patterns corresponding to STO thin films heat treated at various temperatures. Figure 5.7(d) illustrates a well-defined RHEED pattern for STO primarily oriented in the (100) direction in contrast to that shown in figures 5.7(b), 5.7(c), and 5.7(e). According to the RHEED analysis, processing at 800°C and 900°C achieved the (100) orientation, but the degree of orientation is less than that given by 850°C, since the spot pattern intensity is less than that observed at 850°C. At 825°C, the combination ring-like and spot RHEED pattern (faint) of the STO film do not indicate the dominant orientation that was expected. A temperature of 850°C is adequate to achieve epitaxial growth of STO deposited on IBAD MgO. Figure 5.8 shows that the epitaxial nature of the STO thin film was preserved by thermal processing for 2 hours at 850°C.

Identification of the thermal processing time and temperature conditions for STO eliminates only one set of parameters of the processing scheme. Figure 5.9 shows a comparison of two 0.2 M STO thin films heat treated at 750°C under different atmospheres for the crystallization treatment only. The thin film surface appears dense and smooth. A crystallization atmosphere of 1% P(O₂) resulted in a surface roughness of 13 Å while a 10% P(O₂) crystallization atmosphere resulted in a surface roughness of 18 Å. Based on these results, it was determined that the optimum atmosphere for the crystallization heat treatment of the STO thin films was 1% P(O₂).

The rate at which the film ramps up to high temperature plays a strong role in defining the resulting microstructure. Schwartz et al., (8) and Sathyamurthy et al., (25) have suggested

Figure 5.7 RHEED images of the 0.2M STO thin film captured at varying temperatures to determine the optimum crystallization temperature for epitaxial growth. The films were thermally processed as described in the experimental technique prior to the RHEED analysis. A RHEED image of an STO single crystal is provided to illustrate the ideal epitaxial configuration. (a) STO single crystal, (b) 800°C, (c) 825°C, (d) 850°C, (e) 900°C.

Figure 5.8 RHEED images of the 0.2M STO thin film thermally processed at 850°C for varying dwell times. The films were thermally processed as described in the experimental technique prior to the RHEED analysis. (a) STO single crystal, (b) 1 hr., (c) 1.5 hrs., (d) 2 hrs., (e) 3 hrs.

Figure 5.9 Comparison of film microstructure at varying crystallization treatment atmospheres. The heat treatment temperature was 750°C. (a) 0.2 M STO, Pyrolysis atmosphere: 10% P(O₂), Crystallization atmosphere: 1% P(O₂), Average roughness: 13 Å; (b) 0.2 M STO, Pyrolysis atmosphere: 10% P(O₂), Crystallization atmosphere: 10% P(O₂), Average roughness: 20 Å.

that higher ramp rates lead to denser films in the case of STO. Figures 5.10 and 5.11 show the effect of processing ramp rates on the STO thin film. According to Figure 5.10, ramp rates of 50°C/min. and 100°C/min. yield a finer grain size when compared to a ramp rate of 10°C/min. Figure 5.11 provides a visual depiction of the respective surface roughness values that indicates that a higher ramp rate leads to smoother surfaces. The roughness values were 20, 15, and 18 Å for the 10, 50, and 100°C/min. ramp rates, respectively. The 50°C/min. ramp rate was selected as the optimum processing heating rate.

5.4.4 Epitaxial Thin Films

CSD was used to deposit 0.2 M STO thin films on IBAD MgO templates using the established pyrolysis and crystallization conditions to yield high-quality films. The films were pyrolyzed at 200°C for 20 minutes in a 10% P(O₂) atmosphere. The ramp rate to the pyrolysis temperature was set at 1°C/min. Crystallization processing was carried out at 850°C for 2 hours in a 1% P(O₂) atmosphere. The ramp rate to the crystallization temperature was

Figure 5.10 SEM secondary electron images of 0.2 M STO thin film heat treated at 800°C for 2 hours at different ramp rates. (a) 10°C/min. (b) 50°C/min. (c) 100°C/min.

set at 50°C/min. The surface roughness of the films was ~ 10 Å as indicated by AFM analysis. Figure 5.12 shows the XRD θ -2 θ plot for the 0.2 M STO thin films. The presence of only the (200) STO diffraction peak indicates single phase films as well as preferred orientation in the (200) direction. The in-plane texture of the IBAD MgO substrate was $\sim 9^\circ$ and that of the STO films was $\sim 8.6^\circ$.

An $\text{SrCu}_{0.05}\text{TiO}_y$ buffer layer was also deposited onto an IBAD MgO template and thermally processed under the same conditions given for the STO thin film. Figure 5.13 shows the surface morphology of the thin film. The surface roughness of the film was ~ 25 Å.

Figure 5.11 3-D AFM surface images of 0.2 M STO thin films heat treated for crystallization at 800°C for 1 hour at different ramp rates. (a) 10°C/min. (b) 50°C/min. (c) 100°C/min.

The cross-section of the buffer layer/IBAD MgO interface is shown in Figure 5.14. The in-plane texture of the IBAD MgO substrate was $\sim 9^\circ$ and that of the Cu-doped film was $\sim 11^\circ$. As depicted by the IBAD MgO/Cu-substituted STO interface, the ~ 30 nm thick film grows by heterogeneous nucleation.

A thin film of YBCO was deposited onto the Cu-doped STO buffer layer to test continued growth in the (100) orientation. The YBCO deposited onto the spin coated $\text{SrCu}_{0.05}\text{TiO}_y$ buffer layer grew in the (100) orientation with an in-plane texture of $\sim 11^\circ$, similar to that of the buffer layer as shown in Figure 5.15. This sample was not superconductive.

5.4.5 Multiple Thin Film Coatings

Multiple layers of STO were deposited to obtain a thin film thickness >30 nm to

Figure 5.12 XRD data plot of a ~30 nm STO thin film deposited on IBAD MgO by CSD confirming epitaxial alignment in the single phase STO thin films. The diffraction peak at ~43° corresponds to overlapping reflections of the Ni substrate and MgO layer. The peak at ~46° denotes the (200) STO diffraction.

Figure 5.13 SEM micrograph showing the surface morphology of the $\text{SrCu}_{0.05}\text{TiO}_y$ thin film deposited by spin coating.

Figure 5.14 TEM cross-sectional images of the $\text{SrCu}_{0.05}\text{TiO}_y$ thin film deposited onto IBAD MgO by chemical solution deposition. The microstructure of the ~ 30 nm thick film is indicative of columnar type growth.

investigate film thickness effects on T_c . Coated conductors were fabricated with 2, 3, and 6 consecutive layers of STO spin coated onto the IBAD MgO with no intermittent pyrolysis. The films were pyrolyzed after the deposition of the final layer. YBCO was deposited onto the series of STO layers by PLD. The magnetic susceptibility (χ), a quantity indicating the onset of the superconductivity, of each of the coated conductors was measured. Figure 5.16 shows the temperature (K) vs. χ plot. The YBCO film on the 2 STO layers (thickness ~ 60 nm) exhibited weak magnetization over a temperature range of 80-81 K when compared to a strong and sharp transition over less than 1 K at 80 K for the sample with 3 layers of STO (thickness ~ 90 nm). The YBCO film on the 6 STO layers (thickness ~ 180 nm) did not exhibit a T_c . The sharp transition observed for 3 STO layers indicates an increased homogeneity through the sequence of layers when compared to that of the 2 and 6 STO layers. XRD texture measurements showed that the in-plane texture of the 3 and 6 STO layers was $\sim 8^\circ$ and that of the YBCO layer was $\sim 7.3^\circ$ and $\sim 6.97^\circ$, respectively. Figure 5.17 shows the pole

Figure 5.15 Pole figures corresponding to (a) $\text{SrCu}_{0.05}\text{TiO}_y$ buffer layer deposited on IBAD MgO by chemical solution deposition and (b) YBCO superconducting film deposited on (a) by PLD. Both the $\text{SrCu}_{0.05}\text{TiO}_y$ buffer layer and the YBCO are (001) textured out of plane.

Figure 5.16 Magnetic moment curves of (a) 2 STO layers, thickness ~ 60 nm; (b) 3 STO layers, thickness ~ 90 nm; (c) 6 STO layers, thickness ~ 180 nm.

figures associated with the 3 STO layer sample indicating epitaxial growth of the YBCO on the STO.

5.5 DISCUSSION

The degree of film densification increases with faster heating rates due to the retention of a lower viscosity structure to a higher temperature. Maintaining a lower viscosity or a “runny” film at a higher temperature translates to decreased porosity due to the ease of continuous flow when compared to that of a higher viscosity film. The ramp rate also has a direct effect on the type of nucleation event and the resulting grain sizes (8). Columnar microstructures or heterogeneous nucleation results from slower heating rates due to the longer time allowed for complete transformation of the film prior to reaching the thermal input required to overcome the homogeneous nucleation energy barrier. Heterogeneous nucleation followed by columnar type grain growth was observed for the Cu-doped STO thin films at a ramp rate of 50°C/min. Faster heating rates yield microstructures characteristic of both interface and surface nucleation. For the STO thin films, doubling the ramp rate to 100°C/min. resulted in an increase in surface roughness as measured by AFM. This indicated that the film growth proceeded by both heterogeneous and homogeneous nucleation. In the case of faster heating rates, sufficient energy is provided to the system to overcome energy barriers for both heterogeneous and homogeneous nucleation. Prior to full amorphous-to-crystalline transformation via heterogeneous nucleation, the energy barrier for homogeneous nucleation is also surpassed allowing a mixture of nucleation events. It is speculated that surface roughness is related to the type of nucleation event responsible for film crystallization. Smoother surfaces are characteristic of homogeneously dominated nucleation due to greater surface uniformity and finer grain size when compared to that of a film that crystallized by both homogeneous and heterogeneous nucleation.

The extent of texturing in solution deposited thin films depends on the lattice matching between the substrate and the thin film and on thermal processing parameters (26). The

Figure 5.17 Pole figures corresponding to (a) the 3 STO buffer layers deposited on IBAD MgO by chemical solution deposition and (b) YBCO superconducting film deposited on (a) by PLD. Both the $\text{SrCu}_{0.05}\text{TiO}_y$ buffer layer and the YBCO are (001) textured out of plane.

theory of crystallization in traditional glasses can be used to explain the crystallization of thin films with high degrees of texture. According to this theory, the free energy difference, and thus the crystallization driving force, between the amorphous film and the crystalline phase is larger at low crystallization temperatures. The driving force required to initiate heterogeneous nucleation is less than that required for homogeneous nucleation to dominate the film microstructure. Therefore, the lower driving force for crystallization at higher thermal processing temperatures favors nucleation by heterogeneous growth at the substrate. This translates to a higher degree of epitaxy for the thin films. Based on this, fast heating rates that delay film crystallization to higher temperatures should be favored in the selection of a thermal processing scheme. The definition of a “fast heating rate” is dependent on the material system. For the present case of STO thin films on IBAD MgO, a ramp rate of 50°C/min. produces films with a lower surface roughness as measured by AFM. The thin film processed at a ramp rate of 100°C/min. was rougher when compared to that processed with ramp rate of 50°C/min. perhaps due to the doubling of the ramp rate that may have provided a greater thermal input contribution to overcome the barriers for both heterogeneous and homogeneous nucleation events. TEM findings confirmed the relationship between the selected ramp rate and the favored heterogeneous nucleation pathway.

For different chemistries but similar structure and lattice mismatches less than a few percent, film epitaxy results from the growth of small, nanometer sized grains along the substrate/film boundary (20, 26). The shape factor, $f(\theta)$, term taken into account only by heterogeneous nucleation decreases with higher degrees of lattice matching (8, 20). Consequently, the free energy required for nucleation to initiate heterogeneously is less than that for homogeneous nucleation by the factor $f(\theta)$. Thus, choosing the path of least resistance, the thin film will crystallize heterogeneously. Increasing temperatures during thermal processing allow the small grains to grow along the interface and through the film by consuming other randomly oriented grains. The reduction of grain boundary area is the apparent free energy driving force that fuels epitaxial growth.

High degrees of lattice matching are ideal, but are not the limiting factor for epitaxial growth. Morphological instability and abnormal grain growth are responsible for aligned growth of lattice mismatched systems (26). To attain the lowest energy state possible, film growth proceeds through the consumption of randomly oriented grains by abnormal grains with specific orientations once the grain size exceeds the film thickness. Epitaxial films can be obtained from large film/substrate lattice mismatches through more involved processing. A seed layer of the film material deposited directly onto the substrate compensates for the lattice mismatch. The seed layer is initially a polycrystalline film that is thermally processed to break up into individual grains or seeds that will act as heterogeneous nucleation sites on the surface of the substrate. The subsequent film deposited on the seed layer will grow into a columnar morphology on the favorably oriented seeds. Several research efforts have used seed layers to prepare oriented perovskite films (14-20). In contrast, the STO and Cu-doped STO thin films grown in this study were highly oriented, but did not require a seed layer.

Numerous reports in current literature agree on the preparation of epitaxial STO thin films by physical deposition methods such as PLD (27, 28). On the other hand, there is disagreement on the need for seed layer to grow epitaxial STO thin films by CSD (29, 30). Several investigators have documented the growth of oriented STO thin films without the use of a nucleating seed layer (12, 13). This growth behavior was particularly observed in films ~10-20 nm thick which mimic the seeded growth process for a thickness of one film and continue to grow epitaxially following layer-by-layer deposition (13). In this study, the thickness of individual STO and Cu-doped STO thin films was ~30 nm. It may be the case that similar to other studies the films are thin enough to also grow as seed layers. However, the epitaxial nature of the STO and Cu-doped STO thin films shows that it is possible to achieve orientation without a seed layer by CSD.

The practicality of using a seed layer to tailor film epitaxy complicates the processing of thin films and may even be obscured by the additional resources required to successfully

introduce such a layer into the thin film sequence. Optimization of the joining of two materials of dissimilar lattice parameters calls for structure simplicity. For the present case of depositing STO onto IBAD MgO, the ultimate proof of principle was to introduce a single layer of STO by CSD into the YBCO coated conductor structure while maintaining epitaxy and thus, superconducting capability. The use of a seed layer requires a minimum of two STO layers, the nucleating STO seed layer and the epitaxial STO layer. There is the possibility of using the STO seed layer as the single buffer layer in the YBCO thin film sequence if adequate film orientation can be achieved. As demonstrated by the single layer STO and Cu-doped STO films grown in this study, only one layer is required to achieve growth in a preferred orientation. However, the coated conductor fabricated with one buffer layer of composition $\text{SrCu}_{0.05}\text{TiO}_y$ as well as the one with 6 STO layers were not superconductive. This indicates that buffer layer thickness is not the only factor affecting superconductivity.

5.6 SUMMARY

Thermal processing conditions for epitaxial growth of single phase 0.2 M STO and Cu-doped STO thin films on IBAD MgO templates were established. The pyrolysis conditions were 200°C for a duration of 20 minutes in a 10% $\text{P}(\text{O}_2)$ atmosphere. For the crystallization treatment, the films were processed at 850°C for 2 hours in a 1% $\text{P}(\text{O}_2)$ atmosphere. Average roughness values for the STO and Cu-doped STO thin films were $\sim 9 \text{ \AA}$ and $\sim 15 \text{ \AA}$, respectively, as indicated by AFM analysis. XRD analysis showed that the thin films were oriented in the (200) direction suggesting epitaxial growth on the IBAD MgO template. The average texture of the STO films was $\sim 8.8^\circ$ and $\sim 11^\circ$ for the Cu-doped STO films. YBCO coated conductors were fabricated with the STO and Cu-doped STO films as buffer layers. The texture of the YBCO with the STO buffer layer was $\sim 8^\circ$ while that of the YBCO with the Cu-doped STO buffer layer was $\sim 11^\circ$. Textured films were obtained without the use of a nucleating seed layer in contrast to several studies that document the need for a seed layer to obtain films with preferred orientation.

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CONCLUSION

To keep a lamp burning we have to keep putting oil in it.

— Mother Teresa (1910-1997)

Albanian nun, missionary. She devoted her life to caring for lepers and the poor in India; awarded the 1979 Nobel Peace Prize.

6.1 CONCLUDING REMARKS

6.2 FUTURE WORK

6.1 CONCLUDING REMARKS

Research has shown that optimum superconducting properties can be obtained through the use of two buffer layers, ion-beam assisted deposited (IBAD) magnesium oxide (MgO) and $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ in this study. The first buffer layer provides the biaxially aligned template required for oriented growth of subsequent layers. The second buffer layer improves the lattice mismatch between the $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ (YBCO) and the first buffer layer while diminishing the reactivity of the YBCO. The lattice mismatch between MgO and YBCO is 9.67% while that between SrTiO_3 (STO) and YBCO is only 1.5%. Based on lattice parameter alone, it can be speculated that a copper (Cu) doped STO buffer layer should yield YBCO alignment. X-ray diffraction (XRD) analysis confirmed in plane alignment of both the STO and YBCO. TEM compositional analysis revealed that the solubility of Cu in STO was ~1% so a Cu-doped STO buffer layer will not only improve YBCO alignment but it can also minimize Cu diffusion away from the YBCO. A YBCO coated conductor fabricated with a $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ buffer layer deposited by PLD had a critical current density (J_c) of ~1 MA/cm² and a critical temperature (T_c) of ~87 K. The performance of the coated conductor showed that the addition of Cu to the buffer layer is a viable route for saturating the buffer layer with Cu.

Despite the apparent compatibility between the IBAD MgO, the $\text{SrCu}_{0.10}\text{Ti}_{0.90}\text{O}_y$ buffer layer, and the YBCO superconducting film, XRD analysis showed that a $\text{Sr}(\text{NO}_3)_2$ phase was present in the Cu-doped STO powders, especially at higher Cu concentrations. The $\text{Sr}(\text{NO}_3)_2$ was a result of incomplete reaction during processing. Processing conditions for bulk powders must be evaluated to ensure complete reaction of the parent powders to the final desired phase. However, the YBCO coated conductor fabricated with the Cu-doped STO buffer layer had an acceptable J_c and T_c .

PLD of STO results in increased alignment when compared to that of similar buffer layers deposited by CSD. However, this study showed that textured STO and Cu-doped STO buffer layers on IBAD MgO can be obtained by CSD. A significant contribution of this work was that texture of the CSD buffer layer was obtained without the use of a nucleating STO seed layer which has been deemed necessary by several research groups. Epitaxial growth was observed for single layer STO and Cu-doped STO as well as multiple layered samples. Average single layer thicknesses were ~ 30 nm. Growth of epitaxial YBCO films was also achieved on both the STO and Cu-doped STO buffer layers. The texture or in plane alignment (FWHM) after deposition of the STO improved by $\sim 1^\circ$ while it degraded by $\sim 2^\circ$ with the $\text{SrCu}_{0.05}\text{TiO}_y$ buffer. YBCO was deposited by PLD on the STO and $\text{SrCu}_{0.05}\text{TiO}_y$ buffers. The in plane alignment (FWHM) of the YBCO with the STO buffer layer slightly improved while that of the YBCO with the $\text{SrCu}_{0.05}\text{TiO}_y$ buffer layer remained constant. YBCO coated conductors fabricated with one buffer layer of composition $\text{SrCu}_{0.05}\text{TiO}_y$ as well as with 6 STO layers were not superconductive, but did have an 8° in plane alignment. In contrast, coated conductors with two and three STO buffer layers were superconductive. This indicates that buffer layer thickness and epitaxial alignment are not the only factors affecting superconductivity.

6.2 FUTURE WORK

It would be of interest to further study the interaction of the $\text{Sr}(\text{NO}_3)_2$ phase with the Cu-doped STO to investigate the effects of this phase on superconductivity of YBCO coated conductors. Rather than hindering superconductivity, this phase may aid current transport by densifying the Cu-doped STO buffer layer and thus setting up a barrier to Cu diffusion from the YBCO. YBCO coated conductors with varying compositions of the Cu-doped STO buffer layers could be fabricated to study interfacial interactions through the series of films and the possible effects on J_c and T_c .

Results obtained on the CSD deposition of STO and Cu-doped STO show that CSD is a promising fabrication method for buffer layers on IBAD MgO templates. This investigation only touched the tip of the iceberg in CSD deposition of Cu-doped STO buffer layers for YBCO coated conductors. Much remains to be studied and documented. This study failed to investigate the extent of organic removal during the pyrolysis stage of thin film processing. These effects need to be documented in order to establish appropriate thin film processing conditions. The chemistry of the interfacial area shared by the buffer layer and the neighboring IBAD MgO and PLD deposited YBCO needs to be characterized to understand the nature of the material interactions. A study of Cu diffusion would be beneficial to assess the functionality of several Cu doping levels and their effect on coated conductors fabricated by CSD.

Characterization of the buffer layers grown by CSD proved that CSD is a practical route for coated conductor fabrication. In this research the STO and Cu-doped STO buffer layers were processed in two stages, pyrolysis and crystallization treatments, in two different atmospheres, 10% and 1% oxygen partial pressures ($P(\text{O}_2)$), respectively. Buffer layer deposition by CSD can be optimized by reducing the two stages of processing to one combined treatment. Further buffer layer and superconducting film characterization are needed to access the effect of similar processing atmospheres during pyrolysis and crystallization treatments.

THIN FILM DEPOSITION ECONOMICS

Current superconductor use is limited to low temperature superconductor (LTS, $T_c < 60$ K) materials that are used either as small magnets for university research, enormous systems for large laboratory facilities, or in the area of medical diagnosis (magnetic resonance imaging, MRI). However, as technological improvements in computer based and computer related technologies emerge, the electrical demands of society will increase. New businesses such as electric power production, industrial processing, transportation, and medical applications will be based on high temperature superconductors (HTS). Figures A.1 and A.2 show a CO-NECTUS (CONsortium of European Companies Determined To Use Superconductivity) prediction of worldwide market figure demands for superconductivity up to the year 2010 (1). Superconductivity will enter the market with full force. As a consequence, electric generation must also increase. According to Bob Lawrence & Associates, Inc., a Washington, D.C. based firm established in 1986 to focus on technical issues in the areas of energy and the environment, electric generation will on average increase 2.2% per year for the next 20 years (2). An issue that arises due to this foreseen increase is that the electric power grid may be becoming less efficient. The electricity delivered to customers is total generation less 10.6% lost in the transmission and distribution process. Recent analysis shows that in 1997 the difference was 10.13% while in 1998 it averaged 11.05% (2). On a 1 to 1 substitution basis of HTS devices for copper cables, HTS devices will save 1/2 of the present energy losses in

Figure A.1. Market figures represent the annual sales of materials, components and (sub-) systems providing a specific technical function for which superconductivity is indispensable. All after sales services, warranties and related maintenance are included. Commercial orders and pre-commercial orders related to RTD activities, prototype testing and field tests, are included, whereas RTD contracts are excluded. (1)

cables, electric motors, generators, and transformers. A comparison of same cross sections of HTS materials to copper or aluminum materials reveals that HTS materials can carry up to 100 times more current with a virtual absence of resistance. One of the main obstacles to widespread acceptance and application of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) coated conductors is the current manufacturing process. Figure A.3 provides a flowchart of a typical coated conductor manufacturing process coupled with a flowchart illustrating process conditions that need improvement (3). One of the conditions that requires much attention is the thin film deposition rate. In order for HTS to be economically feasible they must be adaptable to large scale production at reasonable costs. Laboratory studies focus on enhancing film

Worldwide Markets for Superconductivity & Market Shares for Low-Tc / High-Tc Superconductors (in M €)				
Business Field	Year 1997	Year 2000	Year 2003	Year 2010
Research & Technological Development (RTD)	355	415	550	840
Magnetic Resonance Imaging (MRI)	1400	1900	2100	2750
TOTAL of RTD & MRI	1755	2315	2650	3590
New Large Scale Applications	35	25	55	980
New Electronics Applications	20	30	75	680
TOTAL of Emerging New Businesses	55	55	130	1660
TOTAL WORLDWIDE MARKET	1810	2370	2780	5250
Market Shares for Low-Tc Superconductors	1805	2355	2730	3650
Market Shares for High-Tc Superconductors	5	15	50	1600

Conectus, December 2001

Figure A.2. As indicated in the table, LTS contributions are predicted to continue their steady growth with a total market share exceeding 3.6 BEUR in 2010. Estimates for HTS are in the range of 1.6 BEUR for 2010. They are based on the forecast that several new businesses will start off in the second half of this decade. We estimate the total market in 2020 may reach 40 BEUR, which corresponds to expected market penetrations of about 15 % in the key fields. In the well established businesses the EU market share is nearly half of the total world market today, whereas the future EU share of value chains in the new fields is currently expected to be considerably smaller. (1)

quality, not on increasing deposition rates. Published literature reports some of the advances that have been recently made in deposition rates. In the case of pulsed laser deposition (PLD), increasing the pulse rate of the laser yielded YBCO coating at rates higher than 1 micrometer per minute (3). The drawback of this modification to the process is the decrease in the size of the laser plume. A single laser would only be capable of coating a few square centimeters of substrate. As a result larger and multiple lasers would be required, thus perhaps increasing the cost of the manufacturing process. Metallorganic chemical vapor deposition (MOCVD) has reportedly achieved deposition rates on the order of 1 micrometer per minute of YBCO coated conductors (3). A drawback of MOCVD is the high cost of precursor metal organic compounds. Electron beam (e-beam) deposition seems promising with nominal rates of 24 nanometers per minute on substrates up to 9 inches in diameter (3).

SUBSTRATE		BUFFER		SUPERCONDUCTOR		PASSIVATION/STABILIZATION/ INSULATION COVERING	
Materials Related	Pretreatment Related	Materials Related	Application Process Related	Materials Related	Application Process Related	Materials Related	Application Process Related
CHEMISTRY & MATERIALS RELATED PARAMETERS							
Compatibility Mechanical Properties Availability Cost Thermal Expansion Magnetic Properties	Rolling Characteristics Texture/Orientation Annealing Surface Roughness Grain Boundary Characteristics	Compatibility Availability Thermal Expansion Chemical Stability Lattice Mismatch Need for Multi- Layers Need for More than One Buffer Cost Diffusion Barrier Oxidation Resistance	Smoothness Continuous/Semi- Continuous Biaxially Aligned Deposition Rate Coating Thickness Material Utilization	Compatibility Precursor Availability Chemical Stability Cost Thermal Expansion Lattice Mismatch Diffusion Barrier	Film Surface Quality Large-Area Coverage Deposition Rate Coating Thickness Continuous/Semi- Continuous Film Stoichiometry Texture/Orientation Achievable J_c , J_0 Values Material Utilization	Compatibility Availability Mechanical Properties Cost Thermal Expansion Oxidation Resistance Electrical Properties	Smoothness Continuous/Semi- Continuous Coating Thickness Reduction in J_c
ENGINEERING & ENVIRONMENTAL BASED PROCESS PARAMETERS							
Process Complexity Energy Needs Controllability Automation Reproducibility Cost Current Status/ Development Needed Scale-up Potential			Process Complexity Energy Needs Controllability Automation Reproducibility Cost Environment Acceptability Safety Waste Management Toxicity & Health Hazards Corrosion Current Status/Development Needed Scale-up Potential		Process Complexity Energy Needs Controllability Automation Reproducibility Cost Environment Acceptability Safety Waste Management Toxicity & Health Hazards Corrosion Current Status/Development Needed Scale-up Potential		Process Complexity Energy Needs Controllability Automation Reproducibility Cost Environment Acceptability Safety Waste Management Current Status/ Development Needed

Figure A.3. Important parameters for continuous processing of coated HTS wires/ribbons. (3)

According to study sponsored by the US Department of Energy (USDOE) and conducted by Sheth and Trembath of the University of Tennessee Space Institute (UTSI), sol-gel based film deposition is economically viable when compared to other fabrication methods (4, 5). This study compared the price per kA m for the following methods: sol-gel, e-beam with RABiTS, e-beam with IBAD, PLD, and MOCVD. Figure A.4 shows the results obtained. The sol-gel and e-beam with RABiTS processing schemes were found to be well within DOE set goals of \$10 per kA m. E-beam with RABiTS was slightly more cost effective than the sol-gel method. Nonetheless, the sol-gel processing method is suitable for the production of quality thin films. One advantage of this method is that it does not require complicated and expensive equipment or high vacuum environments in order to achieve deposition with accurate control over processing conditions. Sol-gel processing can be applied to large-scale production of meter length tapes via dip coating. This manufacturing method would significantly reduce the processing costs involved with HTS. Considering the multilayer structure of the coated conductors, sol-gel methods could be used to deposit one or the entire required sequence of layers.

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Source	Sheth 2002	Chapman 1998	Hammond 1996	Chapman 1998	Chapman 1998
Method	Sol-gel	e-beam w/RABiTS	e-beam w/IBAD	PLD	MOCVD
Production Rate (km/yr)	18,000	18,000	18,000	18,000	18,000
Annual depreciation	10%	10%	20%	10%	10%
Jc (A/cm ²)	1 x 10 ⁶	1 x 10 ⁶	1 x 10 ⁶	1 x 10 ⁶	1 x 10 ⁶
HTSC thickness (m)	4 x 10 ⁻⁶	4 x 10 ⁻⁶	1 x 10 ⁻⁶	4 x 10 ⁻⁶	4 x 10 ⁻⁶
Critical current (A)	400	400	100	400	400
Total capital cost (\$)	32,010,784	30,950,110	59,100,000	88,185,588	33,586,440
Material cost (\$)	17,708,826	8,028,507	3,600,000	11,992,372	7,142,000
Labor cost (\$)	8,836,830	9,013,486	1,800,000	9,974,664	7,142,000
\$/m ¹	2.26	1.71	0.94	3.09	2.26
\$ / kA m	5.65	4.28	9.4	7.72	5.66

Figure A.4. Product cost comparison. (4, 5)

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