

Superconductivity for Electric Systems 2006

Project Summary

PROJECT TITLE:	New Directions in the Deposition of Fluorine-Free HTS Materials
ORGANIZATIONS:	Los Alamos National Lab; Oak Ridge National Lab; Stanford University
PRESENTERS:	Jonathan Storer, Robert Hammond, David Christen
FY 2006 FUNDING:	\$200k (ORNL), \$75K (Stanford), \$300k (LANL)

Project Purpose and FY 2006 Objectives: This project is aimed at materials research and development of a simplified *ex situ* or 2-step *in situ* approach to HTS film synthesis. The approach will develop an economical, scalable, fluorine-free process for coated conductor tape. Compared to the present *ex situ* methods, this approach has potential advantages that could lead to improved throughput and reduced costs, which are needed to fulfill DOE objectives. A key point is that the reaction processing step does not require control of the in-diffusion of water or the build-up and necessary removal of by-product hydrogen fluoride.

- Elimination of the latter limitation could significantly simplify the conversion process, since high gas flow rates or low-pressure processing would be unnecessary; the extension to large volume (batch) processing could be virtually automatic. It may also be possible to match line speeds for deposition and conversion in a reel-to-reel process thereby simplifying the overall process and gaining cost savings.
- Possible expanded compatibility with various classes of lattice-matched buffer layers, possibly including single-layer perovskite-like materials (to date, CeO₂ is the only buffer layer that has shown compatibility with the BaF₂ *ex situ* process,).
- Potentially more economical source materials (metals) are used.

The project involves complementary research efforts at three institutions that span a range of studies from the most basic controlled synthesis on single crystal substrates, by techniques whereby the parameters can best be controlled and individually adjusted, to more practical work on both fixed and moving metal tape substrates. The approach involves:

- Baseline studies using the deposition of fluorine-free precursors by electron-beam co-evaporation of the metals and pulsed laser deposition (PLD). The latter has the advantage of precise composition controlled through target content. The former uses inexpensive metals and can have a virtually unlimited deposition rate over wide areas.
- Reaction to form the HTS layer using different heating and oxygen partial pressure paths into the HTS phase stability regime, adding to the knowledge of phase stability and effect of the liquid BaCu₂O₃ region, and exploring a new process for scale up.
- Processing feedback of YBCO growth development obtained *in situ* using both a high-temperature XRD and FTIR to explore the region of phase stability and growth relative to the liquid-solid demarcation in the phase diagram that includes BaCu₂O₃.
- Further characterization by XRD, SEM, TEM, and electrical properties correlated with post-processing annealing conditions.
- Deposition of precursors and their conversion to HTS materials using reel-to-reel processing. This is a key part of the program as it will guide the way to a truly scalable, commercially feasible process.

FY2006 Objectives:

1. Study processing using two paths: Precursor made by PLD at 300°C, heated at fixed oxygen partial pressure in deposition chamber or a tube furnace, and alternatively, heated in no oxygen to desired temperature followed by oxygen addition into the stability region. The results add to knowledge of phase stability and effect of the liquid region and to exploration of this novel process for scale up.
2. Continue study of growth using the FTIR, to explore the region of phase stability and growth relative to the liquid-solid line.
3. Address the issue of the essentially perfect HTS morphology, which results from the liquid processing, that does not yield sufficient pinning for use in high field. The addition of pinning sites will be studied.
4. Deposit high J_c HTS materials on RABiTS and IBAD-MgO templates using reel-to-reel processing on moving tapes.

FY 2006 Performance:

At Stanford, reacting in tube furnace of low temperature PLD precursors produced similar results as previous XRD dome experiments. From the liquid regime good c-axis growth was obtained. Below the liquid-solid line YBCO did grow, but after one hour the growth was not perfectly c-axis and it contained polycrystalline (a-axis + (103)-oriented) YBCO. A surprising result is that when a PLD precursor with a 1:2:3 composition was used one would not expect to see the effect of a liquid transient. At ORNL, similar explorations using PLD precursors made at low temperature but using a different path were taken to reaction: ORNL heated their samples in reducing forming gas

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then added oxygen at temperature. Measurements of precursor composition, YBCO structure, and superconducting properties were conducted on these samples. TEM was performed both at Stanford and ORNL. Stanford used FTIR to follow the development of the growth using the same process trajectory as at ORNL. LANL made precursors using reel-to-reel processing on RABiTS and IBAD-MgO. Vapor composition during deposition was controlled by atomic absorption sensors. The best YBCO texture was achieved at LANL by a process route that heated the samples first at low (base) pressure then added oxygen rapidly (< 1 sec) to reach the liquid BaCu_2O_3 region before cooling. This result is consistent with the Stanford and ORNL results. Pinning in liquid assisted region was explored by BaZrO_3 additions.

FY 2006 Results:

Key Results from the past year include:

- PLD precursors were ablated from targets of both stoichiometric YBCO and YBCO with 2% BaZrO_3 addition, and the composition of each type of precursor was checked by ICP. For control studies, the precursors were deposited on single crystal LaAlO_3 and CeO_2 -buffered single-crystal YSZ substrates.
- Processing paths of oxygen pressure, temperature, and history were evaluated. Presently the best approach to achieve c-axis oriented, epitaxial films, as verified by all three collaborators, is to introduce oxygen levels to within the YBCO stability region, and near to the BaCu_2O_x liquid-solid boundary field after having heated to the reaction temperature in low oxygen pressure.
- Property measurements of the YBCO films have established low transition temperatures that could be increased only by low-temperature processing in oxygen for long time periods. High-resolution XRD showed continued contraction of the c-axis lattice parameter with annealing duration, and TEM revealed almost no threading defects to permit rapid oxygen diffusion. Microstructure consists of nearly perfectly layered Cu-O planes, with occasional inter-growths of extra Cu-O chains.
- A comparison of structural and superconducting properties has shown improved properties for BZO-doped films, indicating possible beneficial effects of BZO-induced defects for both oxygenation and in-field flux pinning.
- $J_c(H)$ measurements at ORNL on thin films showed $>1 \text{ MA/cm}^2$ (self field; for both BZO and un-doped), with improved field dependence for BZO doping, perhaps due to defects in addition to the Y248 intergrowths seen by TEM in the un-doped YBCO.
- Improved AA sensors to a point that $\pm 2\%$ composition control was routine during reel-to-reel processing.
- Installed and operated an "oxygen pocket" device.
- Developed "tapered sample" method in order to explore temperature dependencies.
- Explored Time-Temperature-Pressure trajectories to produce superconducting samples on tape templates using reel-to-reel methods

FY 2007 Plans:

- Study of the growth of precursors under different paths in the T- P_{O_2} phase field will continue in order to fully understand the phase equilibrium and kinetics of growth and to find the best conditions for process scale-up.
- The use of the XRD dome and FTIR will continue. TEM will be used to show the morphology in detail of both the precursor prior to reaction and of the resultant HTS coating, in order to clarify the precursor phases that are present in the early stages of HTS growth.
- The issue of introducing defects for flux pinning will be explored by a variety of approaches, including nanoparticles such as BaZrO_3 , and spinodal decomposition in solid solution with Nd123 and Sm123.
- Make operational the oxygen pocket demonstration device to produce high J_c YBCO. Investigate rotational speed and deposition rate parameters (thickness per pass) along with O_2 pressure studies.
- Continue to engage the entire team to capitalize on the materials science results in order to produce a 1 meter by 100 ampere tape sample using reel-to-reel methods. This will be a crucial scalability demonstration.

Research Integration:

- There has been fruitful collaboration and information exchange between Stanford, LANL, and ORNL, which has improved our total program capabilities. ORNL and Stanford are working with small single crystals and tape pieces, which are glued with silver paste to a heated metal block. LANL is working with longer lengths of moving tape. Stanford and ORNL are better able to determine the temperature of their substrates and are able to accurately map the pressure-temperature stability plot. This data is being used by LANL to demonstrate the process on moving tape.
- LANL and ORNL, through its CRADA with American Superconductor, have obtained AMSC RABiTS ($\text{CeO}_2/\text{YSZ}/\text{Y}_2\text{O}_3/\text{Ni-W}$). Some of this material was used by Stanford and LANL and results were exchanged between them and with AMSC. In this way, the project is demonstrating the process on a realistic tape substrate.
- LANL has collaborated with ANL to obtain Raman spectra of its YBCO samples.