Technical Memorandum

Ambature TM # 2014 - 03

To: Ron Kelly, CEO, Ambature Corp.

Cc:

From: Davis H. Hartman

Date: 10/01/2014

Re: Growth and characterization of very high-quality a-axis $YBa_2Cu_3O_{7-\delta}$, $NdBa_2Cu_3O_{7-\delta}$, $DyBa_2Cu_3O_{7-\delta}$, and $PrBa_2Cu_3O_{7-\delta}$ thin films

Ron;

We describe in this internal Technical Memorandum (beginning following page) the technical details of our a-axis growth process for YBCO/SLGO films and super-lattices. This description does have variants, but it well describes the mainline growth process. Results are typical, not best or worst cases. With this process we are in position to develop devices for systems applications, such as Josephson Junctions or MRI magnet hardware.

Growth and characterization of very high-quality a-axis $YBa_2Cu_3O_{7-\delta}$, $NdBa_2Cu_3O_{7-\delta}$, $DyBa_2Cu_3O_{7-\delta}$, and $PrBa_2Cu_3O_{7-\delta}$ thin films

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Abstract

We have grown highly-oriented and stoichiometric films of a-axis $YBa_2Cu_3O_{7-\delta}$, $NdBa_2Cu_3O_{7-\delta}$, $DyBa_2Cu_3O_{7-\delta}$, and $PrBa_2Cu_3O_{7-\delta}$, on $SrLaGaO_3$[100] substrates using pulsed laser deposition. X-ray diffraction results indicate that the films are fully a-axis oriented perpendicular to the direction of the substrate and contain as high as 91% b-c plane alignment.

1. Introduction

The $YBa_2Cu_3O_{7-\delta}$, $NdBa_2Cu_3O_{7-\delta}$, and $DyBa_2Cu_3O_{7-\delta}$ cuprate family of superconductors have been extensively studied over the past three decades due to their high critical temperatures (T_c) exceeding 90 °K [1]. These efforts have enabled the development of superconducting devices that can operate at liquid nitrogen temperatures. However, the anisotropic nature of these materials along with their short coherence lengths has impeded device development and subsequent widespread use.

In these materials, the coherence length, which is intuitively the size of the superconducting Cooper pairs, is much longer in the "a" and "b" crystal directions (≈ 2 to 3 nm), as compared to the c-axis direction (≈ 0.7 to 1 nm) [1, 2]. The c-plane has the lowest energy surface plane for these layered structures. Therefore, deposition (a) at high temperatures, (b) at slow-to-moderate growth rates and (c) with a suitable choice of lattice-matched substrate favors the synthesis of high-quality c-axis films [3,4,5]. In contrast, the deposition at high rates and low temperatures reduces the adatom migration length on the film surface. The result is the dominance of growth in the fastest growing direction, which is the a-axis[6]. Under these kinetically limited conditions, growth of a-oriented films is possible and in fact favored [6,2].

Researchers have been able to produce c-axis $YBa_2Cu_3O_{7-\delta}$ films[7] having excellent superconducting properties, using a wide range of growth conditions. These properties include high T_c [8], high critical fields (H_c) [3], and low microwave surface resistances [4]. Use of such films has resulted in development and production of many devices utilizing superconducting transport in the c-axis plane, including bolometers [9] and microwave resonators and filters [10]. However, the very short coherence length in the c-direction, and challenges in controlling interfaces on an atomic scale, have prevented researchers from developing a process that reliably and reproducibly produce vertical tunnel junctions in a stacked multilayer geometry, as has been accomplished with low-T_c Josephson junctions [11].

To produce high-temperature superconductor tunnel devices, most researchers have turned to making junctions with current transport in the a-axis, owing to longer coherence length and better coupling between superconducting layers. In one widely implemented embodiment[12], high-quality c-axis films were etched to produce a ramp, exposing the a-axis. The surface was prepared to form a barrier and then a counter-electrode was deposited. This "ramp type" configuration has produced prototype circuits with a few hundred Josephson junctions [12].

Process uniformity is still the major obstacle to producing useful high temperature superconductor (HTS) circuits with tens of thousands of devices. The low-T_c Josephson junction process has accomplished this[13,14, 15]. However, development of larger more complex HTS circuits awaits needed additional work to reduce the ~8% current spreads characterizing the ramp technology [12].

Fabricating high-quality a-axis films could enable the development of vertical high temperature superconductor Josephson junctions. Previously, the growth of a-axis oriented $YBa_2Cu_3O_{7-\delta}$ and $PrBa_2Cu_3O_{7-\delta}$ has been studied by Eom et al. and Fuchs et al [2,16,17]. Typical growth conditions used to produce a-axis films include these steps;

1. Deposition of a template layer (often a different material such as $PrBa_2Cu_3O_{7-\delta}$) grown at ~ 640 °C;
2. Temperature ramp to a growth temperature > 750° C
3. Post-deposition annealing at higher oxygen pressure [17] on $SrLaGaO_3$ [100] and $SrTiO_3$ [100] substrates

In the text that follows, we describe our unique process for optimizing the production of high-quality a-axis films of the superconductor $YBa_2Cu_3O_{7-\delta}$ and the insulator $PrBa_2Cu_3O_{7-\delta}$. The optimizing involves the use of a low-temperature seed layer in lieu of the buffer layer used by earlier studies[16,17]. We have used the same methods and growth conditions to produce superconducting $NdBa_2Cu_3O_{7-\delta}$ and $DyBa_2Cu_3O_{7-\delta}$, all on (100) $SrLaGaO_4$ (SLGO) substrates. We report the electrical properties of these a-axis oriented films.

2. Growth Methods and Experimental Procedures

We performed our thin-film growth via Pulsed Laser Deposition (PLD) in an ultra-high vacuum cryo-pumped system. We used a 5 Hz, 248 nm KrF-excimer laser (energy density of ~ 0.5 J/pulse) and a target-to-substrate distance of ~ 8 cm. $YBa_2Cu_3O_{7-\delta}$, $NdBa_2Cu_3O_{7-\delta}$, $DyBa_2Cu_3O_{7-\delta}$, and $PrBa_2Cu_3O_{7-\delta}$ were all grown using commercial stoichiometricly sintered targets.

Initially we evacuated the chamber to a pressure of 2×10^{-6} Torr or lower, then flooded it to 125 m-Torr with pure O_2, at a continuous flow rate of 30 SCCM. We found that an initial ~ 450 nm thick seed layer grown with a 640 °C substrate temperature in 125 m-Torr of oxygen produces the films with the highest quality a-axis growth properties. This initial condition is at a significantly lower temperature and a significantly higher pressure than the critical stability lines for tetragonal $Y_1Ba_2Cu_3O_6$ [7,18]. After ~ 6 minutes deposition of this ~ 450 nm thick seed layer, the temperature was raised slowly (while continuing deposition) from 640 °C to 770 °C in ~ 11 minutes. The growth continued for another ~ 50 minutes to attain a total top layer thickness of ~ 450 nm. After growth, the chamber was backfilled to 400 Torr of oxygen, and we cooled the samples slowly to 600 °C, where they remained for more than 60 minutes. Finally, we cooled the films to room temperature over 120 minutes. This final step allows sufficient oxygen incorporation to form the superconducting high-Tc $YBa_2Cu_3O_{7-\delta}$ phase[19].

3. Measurement Methods and Results

We measured material and electrical properties of the a-axis grown films.

Material properties (thickness and composition) of the films were measured using Rutherford Backscattering Spectroscopy (RBS). Alpha particle energy of 3.05 MeV was chosen so that the oxygen content can be accurately measured using Nuclear Reaction Analysis (NRA).

Preliminary resistivity versus temperature (ρ-T) measurements were performed using silver paste contacts in the Van der Pauw configuration with a dipping probe inserted into a 4.2K liquid He dewar.

3.1 Material Properties

We obtained crystallographic information from X-Ray Diffraction (XRD) measurements using an X-Ray mirror, coupled with a 4-bounce Ge monochromator on the incident beam and a 0.09° parallel plate collimator on the receiving optics (PANalytical Model X'pert PRO MRD)[20]. We scanned θ-2θ with Φ= 0° normal to the surface (out-of-plane) to determine the a-axis orientation and the primary and secondary phases present. We inferred the fraction of a-axis orientation from the ratio of the peak areas (θ × counts) of the (100) YBCO peak family to those of the other orientations. In-plane XRD analysis was performed to determine the percent orientation in the b-c plane (in the plane parallel to the substrate surface) [21]. This was done by positioning the diffractometer at a diagonal plane; (102) for $YBa_2Cu_3O_{7-\delta}$, and (104) for $NdBa_2Cu_3O_{7-\delta}$, $DyBa_2Cu_3O_{7-\delta}$ and $PrBa_2Cu_3O_{7-\delta}$. We then rotated the Φ axis and compared the areas of peaks at 90° to each other. If a sample had perfect alignment in the b-c plane, only two-fold symmetry with peaks every 180° would be observed; whereas a sample randomly aligned in the b-c plane would exhibit four-fold symmetry (see Figure 1).

Measurements of the chemical compositions of $YBa_2Cu_3O_{7-\delta}$, $NdBa_2Cu_3O_{7-\delta}$, $DyBa_2Cu_3O_{7-\delta}$, and $PrBa_2Cu_3O_{7-\delta}$ films, inferred from RBS analysis, show that the ratio of the elements fall at $X_{1.00\pm0.02}Ba_{2.00\pm0.02}Cu_{3.00\pm0.02}O_{7.0\pm0.1}$. The $DyBa_2Cu_3O_{7-\delta}$ samples fall within $Dy_{1.00\pm0.2}Ba_{2.00\pm0.02}Cu_{3.00\pm0.02}O_{7.0\pm0.1}$. Previous reports have indicated that optimal superconducting properties for $NdBa_2Cu_3O_{7-\delta}$ are achieved at oxygen growth pressures two orders of magnitude lower than that typically required for $YBa_2Cu_3O_{7-\delta}$[22].

In contrast, we found that high-quality a-axis $NdBa_2Cu_3O_{7-\delta}$ films are achievable with the same oxygen growth pressure for all materials. X-ray diffraction results show that the films grown are highly oriented. The θ-2θ scans indicate a-axis orientations above 99% and orientations in the b-c plane as high as 91 % (see Figure 2).

3.2 Electrical Properties

Electrical measurements were made with the current first sourced along one axis (b-axis); then the other (c-axis). We performed these electrical measurements (principally ρ vs. T) using a computer controlled Quantum Design Physical Property Measurement System (PPMS) cryostat. Contacts were made using SPI High Purity Silver Paint attached to 32 μm-diameter gold wire in the Van der Pauw configuration. The measurements ranged from 50 °K to 310 °K at a cooling rate ≤ 2°K/min and with source currents of 10, 30, 70, and 100 μA. The PPMS was programmed to cool slowly (~ 2 °K /min) to each temperature step, wait for 5 seconds to allow the system to reach thermal equilibrium, perform a measurement at each chosen current value (10μA, 30μA, 70μA, then 100μA) and then continue cooling. After this process was completed, we again repeated the procedure. We recorded data upon both cooling and warming and then repeated the entire procedure on each sample; sourcing current along the b-axes and then the c-axes . Figure 3 shows a representative plot of measured resistivity vs. T

4. Conclusion

We have grown high structural quality a-axis $YBa_2Cu_3O_7$, $NdBa_2Cu_3O_7$, $DyBa_2Cu_3O_7$, and $PrBa_2Cu_3O_7$ films on [100] $SrLaGaO_3$ substrates with a-axis orientation above 99% and orientation in the b-c plane as high as 91%. These a-axis films are potentially useful for applications in high-T_C superconducting devices utilizing vertical transport. We also describe factors that can cause anomalous behavior in the electrical transport measurements of films with anisotropic transport properties and how to minimize their effect.

5. References

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Sample Number/Type	***Film thickness (Å)***	**a-axis orientation (%) ± 0.1 (%)**	**b-c plane orientation (%) ± 0.1 (%)**
YBCO 1	*6,520*	*98.4*	*81.3*
YBCO 2	*6,450*	*41.3*	*72.8*
NBCO 1	*11,680*	*>98 **	*83.4*
NBCO 2	*14,300*	*95.3*	*72.9*
DBCO 1	*7,590*	*86.2*	*87.0*
DBCO 2	*7,310*	*89.1*	*91.4*
PBCO 1	*18,530*	*>98 **	*88.1*
PBCO 2	*11,120*	*88.8*	*51.4*

Table 1: *Plot of measured film thicknesses and the degrees of orientation for a representative sample of grown films. Within the limit of measurement errors, the a-axis alignment is typically in the 90th percentile or better.*

** Measurement error at < 2% misalignment exceeds ±2%*

Sample Number/Type	Transition Temperature b-dir. (K)	Transition Temperature c-dir. (K)	ρ_{90K}/ρ_{300K} b-dir	ρ_{90K}/ρ_{300K} c-dir	ρ_b / ρ_c at 300K
NBCO1	84	-*	1.1	-*	3850
YBCO1	83.5	89.1	0.7	0.816	0.2
YBCO2	88.5	89	1.6	1.900	0.5
PBCO1	n/a	n/a	-	-	-
NBCO2	79.3	87.3	1.0	0.720	30
PBCO2	n/a	n/a	-	-	-
DBCO1	87	87.8	1.5	1.215	150
DBCO2	87.9	89	1.8	1.105	0

*Sample NBCO1 was damaged before c-direction measurements could be performed

Table 2: *Shown are measured transition temperatures and resistivity ratios in the "b" and "c" directions, and the ratio between resistivity in the b and c directions at 300K. We note that* $PrBa_2Cu_3O_{7-d}$ *is a known insulator; the [PBCO1 and PBCO2] films that we grew did not exhibit superconductivity or metallic behavior, as expected.*

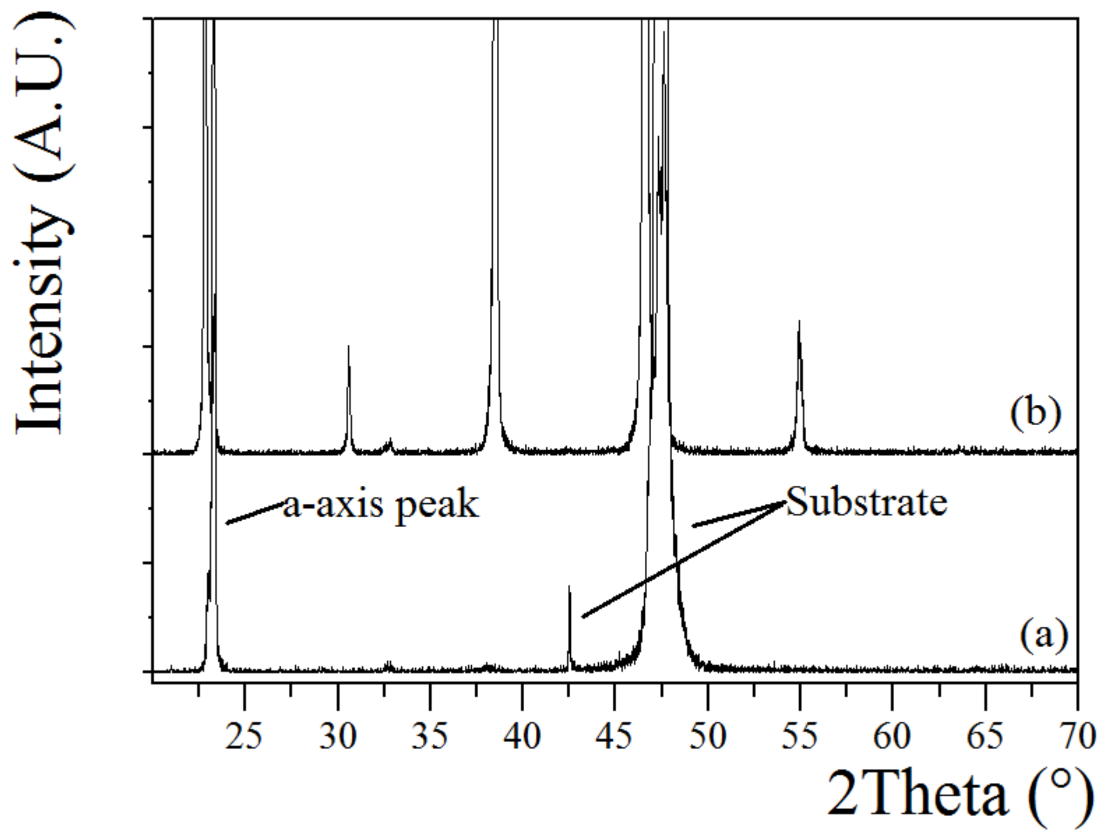

Figure 1: *Overlay of XRD measurements of (a) well-oriented (b) and poorly-oriented a-axis* $YBa_2Cu_3O_{7-d}$*, films. Curve (b) exhibits peaks other than the a-axis and the substrate peaks.*

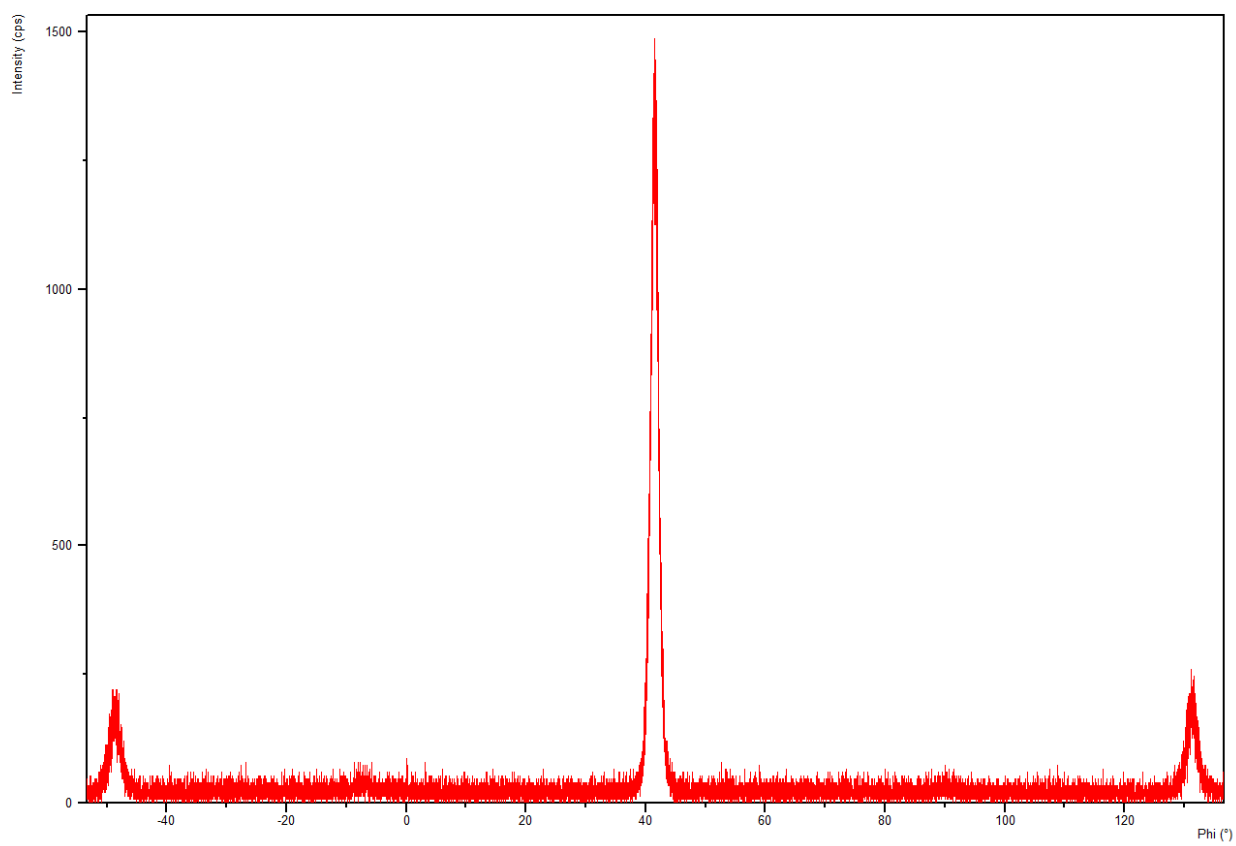

Figure 2: *X-ray diffraction ϕ scan of the (104) plane on a typical* $DyBa_2Cu_3O_{7-d}$*,. The 2-fold symmetry and large difference in peak areas indicates a film with high orientation in the b-c plane.*

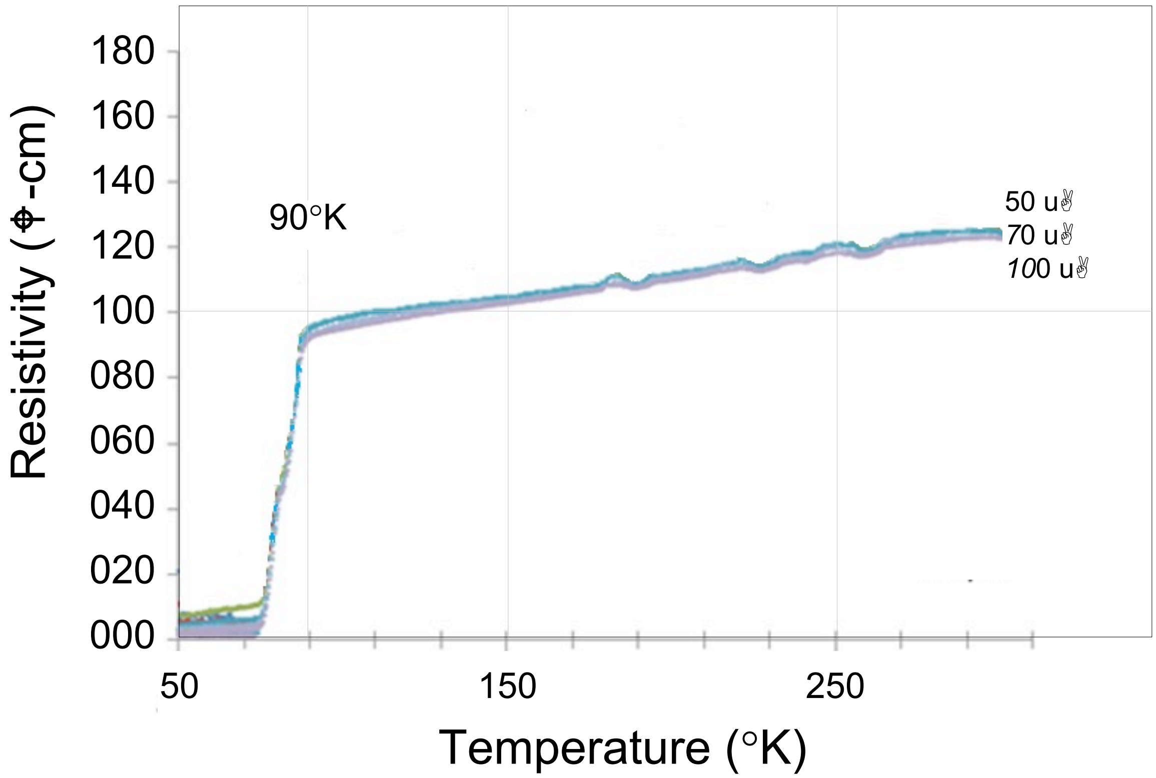

Figure 3: *shows a typical current dependence of the r vs. T plots. This sample consists of a super-lattice of 5 layers each of ~15 nm $YBa_2Cu_3O_{7-d}$ and ~30 nm $NdBa_2Cu_3O_{7-d}$ on a ~450 nm $YBa_2Cu_3O_{7-d}$ a-axis seed layer. A computer-controlled PPMS measurement system was used to make these measurements.*