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In Situ High Rate Growth of High Temperature Superconductor Tapes

Luke S.-J. Peng, Weizhi Wang, William Jo, Tsuyoshi Ohnishi, Ann F. Marshall, Robert H. Hammond, Malcolm R. Beasley, Eric J. Peterson, and Richard E. Ericson

Abstract—*In situ* high rate growth of $\text{YBa}_2\text{Cu}_3\text{O}_{7.5}$ superconducting films has been carried out using e-beam deposition. A deposition flux controller is developed to monitor and control the deposition rates using tunable diode laser based atomic absorption. Wide range of temperatures, deposition rates, and oxygen fluxes including atomic and molecular oxygen, as well as ozone, have been explored in order to understand both kinetic and thermodynamic stability. Critical current density above 1 MA/cm^2 has been achieved on SrTiO_3 substrate samples in growth rate up to 75 Å/sec . Samples prepared on IBAD YSZ/Ni tapes exhibit similar $R(T)$ s and x-ray diffraction patterns. However, critical current densities of the tapes are around kA/cm^2 or lower. The poor critical current density of the tape is attributed to interaction between the $\text{YBa}_2\text{Cu}_3\text{O}_{7.5}$ film and the YSZ buffer layer.

Index Terms—Critical current, e-beam deposition, IBAD, *in situ* growth, phase stability, YBCO superconductor tapes.

I. INTRODUCTION

THE brittleness, porosity, weak-links [1] and misalignment between grain boundaries [2] of the ceramic high temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7.5}$ (YBCO) potentially prohibit it from practical applications. However, recently, the so called coated conductor which uses c-axis epitaxial grown YBCO film onto a flexible, kilometers long metallic tape, has attracted attention throughout the world for potential application in power transportation [3][4]. Among the challenges for economic feasibility consistent with scale-up to industry are growth rate higher than 100 Å/sec over large area, thickness of micrometers, and critical current density J_c greater than 1 MA/cm^2 . The *in situ* e-beam deposition process is believed to be an appropriate technique. However, the molecular oxygen partial pressure required for thermodynamic stability [5]–[7] is too high for e-beam sources and the mean free path is too

restrictive for scale-up. Many have [8][9] proposed that by using the more active atomic oxygen and ozone, the oxygen partial pressure could be reduced by many orders as shown in Fig. 1.

Fig. 1. Oxygen flux vs. $1/T$ plot and thermodynamic phase stability limits. Line $d_1(\text{O}_2)$, $d_2(\text{O}_2)$, and $m_1(\text{O}_2)$ are decomposition and melting lines of YBCO for molecular oxygen [6]. The YBCO phase is stable between d_1 and d_2 . Some well-known processes are indicated. Dashed line $d_1(\text{O})$, $d_2(\text{O})$, and $m_1(\text{O})$ are corresponding suggested decomposition and melting lines of YBCO for atomic oxygen that are many orders lower in oxygen partial pressure. The dashed lines are somewhat arbitrary but our best guess since the atomic oxygen flux is hard to measure accurately. Our works show the YBCO is stable between $d_1(\text{O})$ and $d_2(\text{O})$.

In this paper, we report our attempts at exploring the effects of temperature, deposition rate, fluxes of atomic and molecular oxygen, as well as ozone, in order to understand the growth morphology and the kinetic and thermodynamic phase stability. Investigations are on SrTiO_3 (STO), MgO single crystal substrates and Ion-Beam-Assisted-Deposition (IBAD) Yttrium-Stabilized-Zirconium (YSZ) on Ni alloy tape [3]. Samples prepared at 75 Å/sec growth rate with J_c in

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MA/cm² range have been achieved on STO samples. However, J_c is only in the order of kA/cm² on IBAD YSZ/Ni tapes that is attributed to interaction between the YBCO and the buffer layer.

II. EXPERIMENTS

A. *In situ* e-beam deposition

The *in situ* e-beam deposition technique has been described in our previous paper [8]. Since the conventional chopped-ion-gauge evaporation rate monitor (ERM) is limited above 10⁻⁴ Torr pressure, a tunable diode laser based atomic absorption (AA) sensor has been developed for real-time monitoring and fast PID feedback flux controlling [10]. A wavelength modulated laser beam is shining through the evaporation plume onto a detector. Atomic absorption is then measured by comparing the laser beam that passes through the plume, and the reference beam that splits from the laser source. Since this absorption is proportional to the atomic flux assuming constant velocity in the plume, the vapor flux can be determined. The flux signals are feedback to a PID controller that directs the e-beam power supply to the desired flux level. Unlike the ERM or the quartz crystal monitor, AA sensor is installed outside and is independent of the chamber pressure. Each atomic flux can be resolved from the plume by their individual energy level.

Atomic, molecular oxygen and ozone are used. The atomic oxygen is generated in a microwave-induced discharge chamber. The oxygen flow is introduced through a quartz tube into the vacuum chamber and impinges on the substrates via a Teflon tube. Atomic oxygen flux near the substrate is measured to be 10¹⁴ to 10¹⁶ atoms/cm²-sec. Ozone is generated by an OREC V10-O ozone generator. The O₃-O₂ mixture is fed through a stainless steel tube near the substrates. Ozone concentration is measured to be ~2% in volume in the external flow. However, the true ozone flux at the substrate is undetectable since the flow into the chamber is less than 40 sccm, below the detectable level. Molecular oxygen is supplied through the same tube as the ozone. Flow rate is restricted to 40 sccm because of the limitation of our vacuum system. In either case, the background pressure during deposition is maintained close to 3×10⁻⁵ Torr. We estimate the local pressure at the substrate is ~2×10⁻⁴ Torr when 40 sccm flow rate is used.

After deposition, the chamber is vented to oxygen. The whole cooling cycle after deposition takes about 10 minutes. In general, samples are Y and Cu rich by ~5% by choice. Growth rates in this work are 13-100 Å/sec. Substrate temperature during deposition is 800 to 900°C. Thickness of the film is ~4000 Å.

STO, MgO crystal and sapphire substrates are used. Sapphire is used for ICP analysis. Compositions are found to be the same for the sapphire and the other substrates except for ultra-low oxygen flux case (discuss below). The IBAD YSZ/Ni tapes are provided by Los Alamos National

Laboratory (LANL).

B. Sample characterization

Composition and depth profiles of the samples are analyzed by inductively coupled plasma emission spectroscopy (ICP), Auger electron spectroscopy (AES), SEM, and secondary ion mass spectroscopy (SIMS) at 3M Corp. Resistivity is measured using four-point method in a liquid helium dewar. Critical current is obtained at liquid nitrogen (77K) using Keithley 181 nanovoltmeter and Keithley 228A current source by 1 μV/cm criterion. Crystal structures and phases are characterized by x-ray diffraction (XRD) at Stanford, LANL, and 3M Corp. using Cu K_α radiation. TEM images are taken at Stanford University. Profile fitting of XRD spectra is used to resolve the mixture of phases and possible splittings of each reflection.

III. RESULTS AND DISCUSSION

A. STO and MgO substrates

Below ~830°C, YBCO decomposition is observed when ~10¹⁶ atom/cm²-sec atomic oxygen flux is used where it decomposes into Y₂O₃ and Ba₂Cu₃O_{5,9} [11]. The decomposition line d₂(O) in Fig.1 was suggested by this result. Single phase YBCO with a (103) orientation is obtained when oxygen flux ~10¹⁵ atoms/cm²-sec is used as shown in Fig. 2 (a).

In attempts to establish the decomposition line d₁(O), external oxygen supply is decreased gradually till totally cut off. However, at ~875°C substrate temperature, c-axis epitaxial superconducting YBCO with T_c~86K is observed even without external oxygen supply (to be published). Phase stability in this case is attributed to the atomic oxygen from the STO substrate. SIMS depth profiles show no Ba on sapphire sample while on STO the Ba is constant to the surface. It is well known that oxygen atoms in STO could diffuse to surface and leave vacancies inside crystal at temperature. This oxygen desorption is also enhanced by vacuum, and more by presence of oxygen-active metals at surface such as Y and Ba. Therefore, YBCO could be formed and stabilized on STO substrate. On the other hand, oxygen atoms are not mobile in sapphire, so no Ba is detected. Since the atomic oxygen flux is below the measurable level, the decomposition line d₁(O) remains undefined.

Usage of ozone during deposition gives a similar result as the atomic oxygen. However, the amount that ozone reaches the hot substrates (>800°C) is yet to be determined.

The c-axis epitaxial YBCO appears only when temperature higher than 850°C when deposited with molecular oxygen. The best result comes from temperature at 885±5°C (to be published). J_c > 1MA/cm² at 77K, zero field, has been achieved on 15, 50, and 75 Å/sec deposition rate STO samples. Fig.2 (b) and (c) show selected XRD spectra of samples prepared at 50 and 100 Å/sec, respectively. As can be seen, they are highly c-axis epitaxial. ϕ -scan of pole's

linewidth $\sim 0.74(2)^\circ$ for the highest J_c sample observed implies it is in-plane aligned as well. Profile fittings show splittings on YBCO (001) reflections that correspond to two types of YBCO with different lattice constants: $c=11.680(3)$ and $11.730(5)$ Å, average grain sizes: 5000 and 800 Å, and lattice strains: 0.12(2) and 0.35(5)%. Area ratio of these two types of YBCO is roughly 1:3 (former : latter). Judged by lattice constant [12], their oxygen contents are estimated to be 6.99(1) and 6.82(3). Different types of YBCO are verified by TEM images: faulted YBCO near surface and perfect YBCO at the substrate interface. Fig.3 shows a TEM image of a 50 Å/sec deposited sample. The faulted grains are suspected to carry high currents that require low angle grain boundaries and pinning centers. Thickness of the faulted YBCO is roughly one third of the perfect YBCO that agrees with the XRD area ratio. Further investigations are on the way to explore the correlation between microstructure of the film and its transportation properties. J_c may be much higher when current carrier portion of the YBCO is determined.

Fig. 2. Selected x-ray diffractograms of *in situ* grown YBCO films: (a) 13 Å/sec at 820°C with atomic oxygen, (b) 50 Å/sec at 880°C with molecular oxygen, (c) and (d) 100 Å/sec at 895°C with molecular oxygen. (a) to (c) are on STO substrates, and (d) is on IBAD YSZ/Ni tape. Strong YBCO (103) is found on (a) while (b) to (d) are highly c-axis epitaxial. Secondary phases such as Y_2O_3 , CuO, $Ba_2Cu_3O_{5.9}$ and YBCO-211 are identified in some samples. Y_2O_3 residences in every sample as marked by (). $BaZrO_3$ () is identified in IBAD samples that indicates interaction between YBCO and YSZ buffer layer.

The molecular oxygen partial pressure of our works is

many orders below the well-established decomposition line $d_1(O_2)$ in Fig.1. The phase stability is attributed to the atomic oxygen that perhaps generated by secondary electrons (~ 100 eV) near e-beam evaporator (dissociated from molecular oxygen), or hot molten surface of metal oxides on Ba and/or Y sources (electron stimulated dissociation). However, the process is still unclear. This oxygen flux was estimated to be $\sim 10^{14}$ atoms/cm²-sec in an indirect experiment [13].

Fig. 3. TEM image of a 50 Å/sec *in situ* grown YBCO film on STO substrate. Sample is deposited at 885°C with molecular oxygen (atomic oxygen undetermined). Highly faulted YBCO on top, and defect-less YBCO down below. Secondary phases such as Y_2O_3 and CuO are identified by energy dispersive x-ray analysis

Y_2O_3 particles with 2000-3000 Å diameters are observed. Tentative understanding of growth morphology is as follows [11]: highly active Y atoms react with atomic oxygen forming Y_2O_3 solid along with a liquid phase of $Ba_xCu_yO_z$ flux. The YBCO phase then grows in the $Ba_xCu_yO_z$ liquid flux, nucleating at the substrate [14][15]. This picture is based on Liquid Phase Epitaxy (LPE) by Hirabayashi *et al.* [16] and Tri-Phase Epitaxy (TPE) by Kawasaki *et al.* [17].

Electrical transportation properties of MgO samples are very poor. Measured J_c is less than kA/cm². SEM images show whisker-like pattern on surface that due to hydrolyze of MgO as verified by $Mg(OH)_2$ reflections found in XRD. The surface roughness and the lattice mismatch of the MgO substrate may lead to bad YBCO epitaxial growth and in-plane alignment that result to poor $R(T)$ and J_c .

B. IBAD YZS/Ni tapes

Two batches of IBAD YSZ/Ni tapes are used: with and without CeO_2 cap. $BaCeO_3$ is always found on the later that implies interaction between YBCO and CeO_2 buffer layer. The CeO_2 is known to dissociate above 800°C. Fig. 2(d) shows a typical XRD spectrum from an 100Å/sec *in situ* grown YBCO sample at 895°C with molecular oxygen on YSZ IBAD tape (has no CeO_2 cap). As can be seen, strong (001) reflections indicate it is highly c-axis epitaxial. $BaZrO_3$ is identified that suggests the YSZ buffer layer also dissociates at temperature. Fig.4 shows a SIMS depth profile of a tape sample. As can be seen, the Zr diffuse out into YBCO buffer layer then forming $BaZrO_3$.

Fig. 4. SIMS depth profile of an IBAD YSZ/Ni tape sample that using 5kV Cs⁺ ion. Sample is prepared at 100 Å/sec, 895°C with molecular oxygen. Zr can be found in YBCO film that indicates interaction between YBCO and YSZ buffer layer. Ni also diffuses into YSZ buffer layer. Long tail of each element to right is partially due to kick-in by ion bombardment.

R(T)s of these YBCO tapes exhibit similar features as the STO samples at the same run. However, J_c is only in the order of kA/cm² or lower. X-ray ϕ -scan on eight selected tapes that extend over 40-100 Å/sec growth rate shows an average FWHM~13° of each pole, and non-zero between poles, that indicate poor in-plane alignment. Therefore, YBCO is indeed incorporated into secondary phases and poor in-plane aligned. The result is weak-links between grain boundaries that depress the J_c significantly. Fig.5 shows a ϕ -scan from an 85 Å/sec *in situ* grown tape sample that deposited at 895°C with molecular oxygen.

Fig. 5. X-ray ϕ -scan of an *in situ* grown YBCO on IBAD YSZ/Ni tape that deposited at 895°C, 85 Å/sec with molecular oxygen. The scan is over YSZ (111) and YBCO (103) peak, respectively. Linewidth of each pole is as indicated. Non-zero between poles for YBCO suggests poor in-plane aligned grains.

IV. CONCLUSION

In situ YBCO superconducting films have been grown on STO, MgO, and IBAD YSZ/Ni substrates. Growth rate 13-100 Å/sec, 800-900°C substrate temperature, fluxes of atomic and molecular oxygen, as well as ozone, have been explored. Thermodynamic phase stability is attributed to the presence

of atomic oxygen during deposition. Decomposition limits of YBCO for atomic oxygen are not yet determined. Critical current density ~1 MA/cm² has been achieved on STO samples up to 75 Å/sec growth rate. Microstructure of YBCO together with Y₂O₃ observed suggest the growth is in a Ba_xCu_yO_z liquid flux. Both of the YSZ and the CeO₂ buffer layers on IBAD YSZ/Ni tapes will dissociate at temperature then react with YBCO. The destruction of buffer layer leads to secondary phases and poor in-plane aligned YBCO grains that depress the J_c significantly. A temperature stable buffer layer is required for this high temperature, high rate growth. The alternative is to reduce the atomic oxygen flux during deposition as well as the temperature. However, a sensitive atomic oxygen monitor that capable to detect oxygen flux below 10¹⁴ atoms/cm²-sec level will be needed.

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