Growth and characterization of La$_2$Zr$_2$O$_7$ buffer layers deposited by chemical solution deposition

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Abstract

The deposition and characterization of La$_2$Zr$_2$O$_7$ thin films deposited by metal-organic decomposition method on both single crystal SrTiO$_3$ and cube textured Ni-5 at.%W substrates are presented. Metal acetylacetonates in propionic acid solution was used. The results showed that LZO films are epitaxially grown with smooth surface with rms roughness around 2 nm. YBa$_2$Cu$_3$O$_{7-\delta}$ films, deposited by pulsed laser deposition technique on LZO buffer layers, showed critical temperature of 90 K and critical current density in self magnetic field $J_c = 1.6$ and 13 MA/cm$^2$ at 77 K and 4.2 K, respectively. A better $J_c$ retention in magnetic field for YBCO films deposited on LZO/STO than YBCO on bare STO is observed indicating a rather strong vortex pinning as confirmed by microwave measurements.

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Keywords: La$_2$Zr$_2$O$_7$ buffer layers; chemical solution deposition; YBCO film; coated conductors

1. Introduction

ReBa$_2$Cu$_3$O$_{7-\delta}$ (ReBCO, Re = Y and rare earths) coated conductor (CC) tapes are promising for superconductor – based applications in electric power devices operating at high magnetic field and high...
temperature conditions up to the liquid nitrogen temperature. CCs consist of a highly textured ReBCO film deposited on a flexible metallic tape surface through thin film deposition methods [1]. The introduction of a buffer layer between the metallic substrate and ReBCO film is required for the physico-chemical optimization of the superconducting film performances. The role of the buffer layer, which usually consists of several biaxially textured oxide layers [2], is to prevent chemical contamination of ReBCO film from the substrate elements as well as to adapt the thermal, chemical and crystalline properties of the metallic substrate to those of the YBCO ceramic film. Currently, one of the primary issues consists of the development of a reliable and economically viable long-length production process for coated conductor commercialization. It is recognized that this goal can be achieved with the employment of chemical solution deposition (CSD) methods for both ReBCO and buffer layer depositions [3]. Due to its good chemical compatibility and low lattice mismatch with YBCO, the La2Zr2O7 (LZO) thin films grown by CSD are of great interest buffer and/or seed layers in the fabrication of low cost coated conductors [4]. The CSD, comprising methods such as sol-gel routes and metal-organic deposition (MOD), offers a number of advantages over the vapor deposition techniques. The CSD methods [5] are versatile, non-vacuum methods that do not require expensive equipments and allow an easy control of stoichiometry, suitable for large scale fabrication.

In this article, we report on the growth of epitaxial LZO films on both single crystal SrTiO3 substrate and biaxially textured Ni-5 at.%W (NiW) metallic substrates by a simple chemical solution route using a coating solution obtained by dissolving the La and Zr acetylacetonates in propionic acid. Textured LZO films were obtained after high temperature crystallization treatment up to 950 °C under air and reducing (Ar + 4 % H2) atmosphere. C-axis oriented LZO films were also obtained on NiW substrate. YBCO films deposited on LZO-buffered STO substrates exhibited critical temperature as high as 90.3 K and critical current density $J_c = 1.6$ and $13$ MA/cm$^2$ at 77 K and 4.2 K, respectively. A better $J_c$ retention in magnetic field for YBCO films deposited on LZO-buffered STO than YBCO on bare STO is observed.

2. Experimental

The precursor solution for the deposition of epitaxial LZO thin films has been prepared at room temperature starting from lanthanum (III) 2,4-pentadionate and zirconium (IV) 2,4- pentadionate with a purity of 99.9% provided by Alfa Aesar. They were separately dissolved in an excess of propionic acid (CH$_3$CH$_2$COOH) and mixed in stoichiometric quantities corresponding to La:Zr = 1:1 ratio. The as-obtained solution was concentrated by distillation up to 0.4 M concentration. The LZO precursor solution were deposited by spin coating on both (001)STO single crystal and {100}〈100〉 biaxially textured NiW substrates at a spinning rate of 4000 rpm for 60 s in air. Details on alloy preparation as well as cube texture development can be found elsewhere [6]. The thermal treatment of the as-deposited precursor films was carried out at temperature as high as 950 °C in both air and Ar + 4 % H2 (Ar/H2) flowing atmosphere (20 l/h) for 30 min. The warm up rate was and cool down rates were fixed at 10 °C/min and 20 °C/min, respectively.

The crystalline properties of the films were investigated by x-ray diffraction (XRD) using a Rigaku Geigerflex diffractometer with Cu Kα radiation. The surface of the films was analyzed by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) using a LEO 1525 field emission high resolution scanning electron microscope and a Park XE 150 operating in non contact mode, respectively. The values of root-mean square roughness are obtained from $1 \times 1 \mu$m$^2$ scan area.

YBCO films were grown by pulsed laser deposition (PLD) technique using a 308 nm XeCl excimer laser (Lambda Physik 110i). More details on YBCO deposition conditions can be found elsewhere [7]. D.c. transport measurements were carried out by the four point method on 1 mm long and 30 µm or 50 µm wide strips obtained by standard UV photolithography and wet etching. The field-dependence of the
microwave complex resistivity was measured on YBCO/LZO sample at 48 GHz with the Dielectric Resonator technique [8]. In-plane currents were excited, and the magnetic field $\mu_0H < 0.8$ T was applied perpendicular to the film plane. The complex resistivity shift $\Delta\rho_1+i\Delta\rho_2$ was obtained from measurements of the shift of the $Q$ factor and resonant frequency $\nu_0$ of the resonator. Within general models for vortex motion without flux creep [9], one finds $r = \nu_p/\nu$, where the depinning frequency $\nu_p = k_p/\eta$ and $k_p$ and $\eta$ are the pinning constant and vortex drag coefficient, respectively.

3. Results and discussion

3.1. LZO films on STO substrate

LZO films on STO substrate were obtained at different annealing temperatures, $T_a$, under both static air and flowing Ar/H$_2$ reducing gas conditions as summarized in Table 1.

XRD $\theta - 2\theta$ measurements revealed a c-axis preferential growth for all the samples. In figure 1, the pattern recorded on sample S1 ($T_a = 950$ °C in static air) is reported showing very sharp and intense (00l) peaks and minor (222) reflection. In addition, reflections related to other phases were not detected. These features are typical of all the LZO/STO samples annealed at both $T_a = 900$ and 950 °C independently of the gas processing conditions. The rocking curves measured on the (004) LZO peaks revealed a valuable reduction in the Full Width at Half Maximum (FWHM) for samples processed in Ar/H$_2$ atmosphere (see values reported on Table 1). Taking into account that all the measured curves exhibited a purely lorentzian-like intensity distribution (see the inset of figure 1), it can be demonstrated that the FWHM is inversely related to the in-plane x-ray coherence length rather than to the out-of-plane film mosaicity [10]. The reduction in the FWHM is then likely ascribed to an elongation in the LZO in-plane x-ray coherence length. This, in turn, means a reduced density of crystalline defects - such as misfit and edge dislocations, vacancies and stacking faults - in film processed in flowing Ar/H$_2$ at 950 °C.

In figure 2 the SEM image of the S3 LZO films deposited on STO substrate is shown. This analysis reveals that the LZO film grown on STO shows a smooth surface free of cracks and particulates. Nevertheless, few voids due to incomplete grain coalescence can be observed. Grain boundaries regions can be discerned as well. The root mean square roughness, $R_{rms}$, and the grain size are of about 2.7 nm and 60 nm, respectively, as revealed by AFM images (inset of Fig. 2). Analysis of the sample S1 ($T_a = 950$ °C in air, not shown) revealed reduced roughness to $R_{rms} = 2.1$ nm mainly due to a better coalescence among grains and the reduced grain boundary depth. Conversely, LZO film crystallized in Ar/H$_2$ atmosphere (S4) revealed an unexpectedly small average grain size (around 25 nm).

Table 1. Processing conditions (annealing temperature, $T_a$, and gas composition), FWHM of the XRD (004) peaks rocking curves and the surface rms roughness, $R_{rms}$, evaluated from AFM investigations for LZO samples on STO substrate. Sample M4 is the LZO film grown on NiW substrate.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_a$ (°C)</th>
<th>Gas</th>
<th>FWHM (°)</th>
<th>$R_{rms}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>950</td>
<td>Air</td>
<td>0.76</td>
<td>2.1</td>
</tr>
<tr>
<td>S2</td>
<td>950</td>
<td>Ar + 4 % H$_2$</td>
<td>0.49</td>
<td>---</td>
</tr>
<tr>
<td>S3</td>
<td>900</td>
<td>Air</td>
<td>0.82</td>
<td>2.7</td>
</tr>
<tr>
<td>S4</td>
<td>900</td>
<td>Ar + 4 % H$_2$</td>
<td>0.62</td>
<td>2.6</td>
</tr>
<tr>
<td>M4</td>
<td>950</td>
<td>Ar + 4 % H$_2$</td>
<td>5.9 (4.8 (°))</td>
<td>2.6</td>
</tr>
</tbody>
</table>

(*) FWHM of the (002)NiW RC
Fig. 1. XRD $\theta$ - $2\theta$ pattern recorded on LZO film grown on STO substrate (sample S1). LZO peaks are labelled whereas substrate peaks are marked by *. Inset: RC of the (004)LZO peak. The bolder dashed line is the fit obtained by the lorentzian function.

Fig. 2. SEM picture (200 k) of LZO film grown on STO substrate (S3 sample) surface morphology. In the inset the AFM image for the same sample on a $1 \times 1 \mu m^2$ area is reported.

3.2. LZO films on NiW metallic substrate

In figure 3 XRD pattern of the LZO film growth on NiW metallic substrate is shown. The pattern mainly shows the (004) peaks, indicating $c$-axis oriented LZO coatings. Nevertheless, the presence of low intensity (222)LZO reflection reveals the presence of polycrystalline component. The peaks intensity ratio $I(004)/[I(004)+I(222)]$, which is an estimation of the volume fraction of the epitaxial grains, is about 0.7. This ratio can range between 0.375 and 1 corresponding to randomly oriented and fully (00$l$)-oriented LZO films, respectively [11]. The FWHM of the RC for (004)LZO peak measured along the substrate rolling direction is 5.9° close to that of the NiW substrate (4.8°). The occurrence of such a polycrystalline fraction can be only partially attributed to the film grown on non-cube oriented or cube-twinned grains, actually present as a minor component in NiW substrate. No cracks were observed by SEM investigations.

3.3. YBCO films on LZO/STO

YBCO films were deposited by PLD on both S1 and S3 LZO/STO samples. From XRD measurements YBCO films resulted epitaxially grown on LZO with the (005)YBCO RC FWHM = 0.83°.

The SEM image reported in figure 4(a) reveals a very flat and compact YBCO film surface. The grain coalescence is complete and a few holes and voids can be detected. Small density of droplets and secondary phases or outgrowths can be also appreciated on the film surface. High critical temperature ($T_c$ (R=0) = 90.3 K) was measured by d.c. resistive method with sharp resistive drop at $T_c$ (not shown) indicating the homogeneity of the YBCO film. Moreover, the resistivity values (330 and 120 $\mu$Ω cm at 270 K and 100 K, respectively) and its $T$-dependence are in agreement with good quality epitaxial YBCO films grown on single crystal substrates.
Fig. 3. X-ray diffraction $\theta - 2\theta$ pattern recorded on LZO film grown on NiW metallic substrate (sample M4). LZO peaks are labelled whereas substrate peaks are marked by *. The Intensity is report in log scale in order to emphasize the low signal component of the spectrum.

Fig. 4. (a) SEM image; (b) $J_c(B)$ dependences for YBCO epitaxial films deposited on LZO/STO (diamonds) and STO (circles). Inset: $J_c(T)$ dependence for YBCO/LZO/STO sample.

In figure 4(b) the normalized $J_c(B)$ curve at 77 K is plotted. A similar curve measured for a typical YBCO epitaxial film on STO is also shown for comparison. As can be seen YBCO on LZO shows a different dependence with a better $J_c$ retention with increasing field. This results in a higher irreversibility field for YBCO on LZO/STO ($H_{irr} = 8.3$ T instead of 6.7 T). The temperature dependence of the critical current density, $J_c$, in zero field is plotted. High $J_c = 1.6$ and 13 MA/cm$^2$ were measured at 77 K and 4.2 K, respectively. Figure 5 reports the field-increase of the 48 GHz microwave complex resistivity $\Delta \rho_1 + i \Delta \rho_2$ as measured with a dielectric resonator [8] at the technologically interesting temperature $T = 79.8$ K, together with the field dependence of the the pinning parameter $r = \Delta \rho_2 / \Delta \rho_1$. This is an important parameter to assess the strength of pinning being a measure of the ratio between the reactance (elastic response) and resistance (dissipation) given by vortices. An initial downward curvature in $\Delta \rho_1 + i \Delta \rho_2$ could be ascribed to the effects of grain boundaries or twin planes, giving rise to Abrikosov-Josephson vortices, that however seem to be strongly pinned (see inset). At higher fields, $\Delta \rho_1 + i \Delta \rho_2$ evolves toward a linear field-dependence, typical of conventional Abrikosov vortices. The pinning parameter has a field dependence typical of good YBCO samples [12], with absolute values pointing to rather strong pinning.
Fig. 5. Field dependence of the microwave complex resistivity. Inset: $r$ parameter (see text), indicating a depinning frequency in excess of 45 GHz at low fields.

The evaluated \[ \nu_p = 44 \text{ GHz at } 0.5 \text{ T} \] is comparable to \[ \nu_p = 60 \text{ GHz at } 0.5 \text{ T} \] in YBCO with BaZrO$_3$ inclusions [12].

4. Conclusions

In this article, the growth of epitaxial LZO films by CSD method on single crystal SrTiO$_3$ substrate is reported together with first attempts on biaxially textured NiW metallic substrates. Textured LZO films were obtained after high temperature crystallization treatment up to 950 °C under air and Ar + 4 % H$_2$ atmosphere. As for NiW substrates, even tough further studies are required, c-axis oriented LZO films were also obtained. YBCO films deposited on LZO-buffered STO substrates exhibited critical temperature as high as 90.3 K and $J_c = 1.6 \text{ MA/cm}^2$ at 77 K. From both d.c. and microwave measures rather strong pinning is observed in YBCO on LZO/STO.

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