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$La_2Zr_2O_7$ films on Cu–Ni alloy by chemical solution deposition process

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Abstract

Films of $La_2Zr_2O_7$ (=LZO) have been formed by chemical solution deposition technique (CSD) on new bi-axially textured Cu–Ni alloy tapes based on rolled constantan ($Cu_{55}Ni_{45}$) Rabits. The precursor used was acetylacetonates treated in propionic acid (0.1–0.87 mol/l) and then deposited by spin-coating. The LZO film starts to crystallize above 850 °C, the film nucleates bi-axially textured on the substrate (with unit cell axis rotated 45° from those of the substrate). The top part of the film is not textured even after long annealing time at 1100 °C, but the interfacial part is bi-axially textured. Thus, synthesis of bi-axially textured films on $Cu_{55}Ni_{45}$ Rabits seems possible but more works are needed to optimize its properties.

Keywords: Texture; Solution deposition; Oxide film; Lanthanum zirconate

1. Introduction

Thin oxide films have increasing importance for functional or structural applications and sustain a considerable attraction in the material science community. Coating metal based tapes with thin oxide films was initiated by coated conductors studies for superconducting cables applications but this range will broaden in other fields when long length of flexible materials with interesting properties could become available. For example, multilayer capacitors applications require deposition of dielectric films on metal tapes. Recently, Nb doped $SrTiO_3$ deposited on bi-axially textured Ni Rabits (rolled assisted bi-axially textured substrates) have been used to form multilayer capacitors [1]. Deposition of ion conducting oxide electrolyte on metal such as Ni could be an efficient starting point for making solid state fuel cell using thin films and then working at moderate temperature. One key problem is to achieve high or even full densification of the film at the lowest possible temperature; this is not an easy task when polycrystalline films are concerned. However, if the substrate is a single crystal or a bi-axially textured material with a low structural mismatch with the film, then the film can grow coherently and this epitaxial phenomenon becomes an important ingredient of the densification process that can occurs at a quite low temperature ($0.3T_{melting}$) [2,3].

During the last years, many efforts have been focused on $YBa_2Cu_3O_7$ (YBCO) coated conductors because YBCO is the best candidate for a second generation of superconducting cables [4]. YBCO coated conductor is composed of a bi-axially textured YBCO film deposited on a metallic substrate with intermediate buffer layers. These buffer layers have three essential functions: (i) firstly to act as a chemical barrier preventing diffusion of metallic elements into YBCO; (ii) secondly preventing oxidation of the metallic substrate during YBCO film processing that involve a step at high temperature under oxygen; (iii) finally to transfer the texture from the substrate to YBCO. YBCO needs to be bi-axially textured to have high J_c capacities that depends strongly on crystallographic orientation [5]. Up to now, many oxides films performed by chemical solution deposition (CSD) method have been investigated for buffer layers on Ni based substrates: CeO_2 [6], Y_2O_3 stabilized ZrO_2 (YSZ) [7], $La_2Zr_2O_7$ (LZO) [8–10].

Face centered cubic (fcc) metals, like Ni, Cu, Al among others, can easily form cube texture by deformation (rolling) and annealing. Because Ni is more easily textured and less oxidizable it was the preferred one. In particular, many efforts have been made on Ni–W alloys because of its highly stable texture and acceptable mechanical properties for long tape applications. Several Ni-based alloys (Ni–W, Ni–Cr and Ni–Cu) have been

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developed in order to decrease its Curie temperature below the working temperature of coated conductors (77 K) and minimize ac losses. Compared with Ni, Cu and Cu-based alloys can be textured by thermo-mechanical process [11,12], but are not ferromagnetic and which is attractive to decrease ac losses. But Cu has some disadvantages, such as poor thermal stability of texture and poor oxidation resistance. To overcome the disadvantage of the later one, a special buffer architecture is necessary [13]. Recently, Cu–Ni bi-axially textured tapes were produced [14] that could be interesting to test as potential substrates.

Chemical solution deposition method [15] is a class of non-vacuum methods that does not require expensive equipments, it is also versatile thanks to chemistry and it allows an easy control of stoichiometry. This anticipates large fabrication scale. There are mainly two CSD approaches: sol–gel processes and metal–organic deposition (MOD) differing in their principle. Sol–gel processes usually start form metal alkoxide (or transformed alkoxide) and proceed by inorganic polymerization through controlled hydrolysis, they provide nanometer scale particles that can be deposited as a film. MOD processes start from metal carboxylates or metal β-diketonates solutions; the solution is deposited directly on the surface and reticulated thanks to assembling properties of the precursor. Pyrolysis and crystallization of oxide are performed by heating, typically above 600 °C. These processes have high potentialities to make thin and smooth films by dip-coating, spray-coating or spin-coating. CSD processes have generally a high deposition rate compared to physical-based processes.

High temperature annealing is often required to crystallize buffer layers by CSD method, in certain cases, a temperature higher than 1100 °C [6]. That is why many studies were performed on Ni–W Rabits to fabricate buffer layers for coated conductor by this technique. Recently, cube-textured LZO buffer layers fabricated at lower temperature (900 °C) were reported [8,9]. This result motivated us to investigate fabrication of LZO on other non magnetic substrate by CSD. We choose to work on the newly available bi-axially Cu–Ni based alloys [14].

In this paper, we focus and discuss on how to obtain cube-textured LZO layers on $Cu_{55}Ni_{45}$ alloy and have mainly investigated: (i) a deposition process of LZO by CSD, (ii) preliminary studies on annealing temperature and annealing time; (iii) the role of concentration of the solution; (iv) the texture formed and the microstructure of the films. Based on these results, we discuss how cube-texture of LZO film could be fabricated on the Cu–Ni alloy by CSD process.

2. Experimental

2.1. Preparation of solutions

Lanthanum(III) 2,4-pentanedionate ($La(acac)_3$) and zirconium(IV) 2,4-pentanedionate ($Zr(acac)_4$) were used as precursor compounds. Based on weight losses measurements, our $La(acac)_3$ contained $3H_2O$ per formula unit. It was difficult to dissolve $La(acac)_3$ and $Zr(acac)_4$ in usual organic solvents such as trichloromethane ($CHCl_3$), tetrahydrofuran (THF), toluene, *N*,*N*-dimethylformamide (DMF), pyridine. For example, pyridine was able to dissolve only 0.01 mol/l of $La(acac)_3$. Because acetylacetone could ionize in aqueous solution as a weak acid:

$$CH_3COCH_2COCH_3 \leftrightarrow H^+ + CH_3COCHCOCH_3{}^-$$

$La(acac)_3$ and $Zr(acac)_4$ are weak acids salts and therefore expected to be soluble in carboxylic acids. Two kinds of carboxylic acids were tested: acetic acid ($C_2H_5O_2$) and propionic acid ($C_3H_6O_2$). Rather high concentration of $La(acac)_3$ and $Zr(acac)_4$ was soluble in acetic acid (>1 mol/l) but the solution tends to form gels rather soon (a few days). Propionic acid was investigated next. By adding a stoichiometric mixture of $La(acac)_3$ and $Zr(acac)_4$ to propionic acid, one obtains after a couple of hours under stirring and heating (at 60 °C), a transparent yellow solution. Based on formal reactions, 1 ml of propionic acid should be able to react with 0.84 g $La(acac)_3$ and 0.93 g $Zr(acac)_4$, but we could not get such high concentration. Instead, we found that the maximum concentration was close to 0.87 mol/l (with respect to La^{3+}), at ambient temperature. In the following, we used $La(acac)_3$ and $Zr(acac)_4$ reacted with propionic acid.

2.2. Preparation and characterization of samples

Cube-textured Cu–Ni substrates were prepared by rolling and annealing commercial ingots of $Cu_{55}Ni_{45}$ with additives like Mn and Fe (∼1 at% each) according to a process published elsewhere [14]. The substrates 5 mm × 5 mm were cut from larger samples, cleaned by acetone for 10 min in an ultrasonic bath, and then spin-coated (rotation speed 2500 rpm, rotation time 30 s, acceleration 3000 rpm/min with the solution. After spin-coating, all samples were dried at 150 °C for 30 min in air. Finally, the samples were heated under Ar-H_2 (5%) flow to avoid oxidation of the substrate and to crystallize the oxide. All the samples were characterized by X-ray diffraction (Cu Kα) using a four-circle diffractometer (Siefert MZ IV using Xenocs multilayer optics). In the following, 2θ is the Bragg angle, ω is used as $2\theta/2$, ϕ characterizes in plane rotations and χ concerns tilts of the sample with respect to the diffusion vector. $\theta - 2\theta$ scans (at $\chi = 0$), ω scans, ϕ scans and pole figures were measured on several samples. The microstructure of LZO films was investigated by SEM (Zeiss ultra 55) and EDX (Jeol-840) was used to check the stoichiometry. Thermal analyses were performed under Ar flow (Setaram TAG 1600, Lyon-France).

3. Results and discussion

3.1. Effect of temperature annealing

CSD process can be divided in two steps [3,15]: pyrolysis and crystallization. The pyrolysis takes place when the organic molecules degrade, this occurs at a moderate temperature (<600 °C), it provides nano-sized particles or amorphous phases that crystallize with increasing temperature. From Fig. 1, it is seen that LZO Bragg peaks were only found above 950 °C with increasing intensity while raising temperature. At the highest annealing temperature, i.e., 1100 °C, no impurities were detected by X-ray suggesting a good compatibility between LZO