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Surface defects on the $Gd_2Zr_2O_7$ oxide films grown on textured NiW technical substrates by chemical solution method

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ABSTRACT

Epitaxial growth of oxide thin films has attracted much interest because of their broad applications in various fields. In this study, we investigated the microstructure of textured $Gd_2Zr_2O_7$ films grown on (001) ⟨100⟩ orientated NiW alloy substrates by a chemical solution deposition (CSD) method. The aging effect of precursor solution on defect formation was thoroughly investigated. A slight difference was observed between the as-obtained and aged precursor solutions with respect to the phase purity and global texture of films prepared using these solutions. However, the surface morphologies are different, i.e., some regular-shaped regions (mainly hexagonal or dodecagonal) were observed on the film prepared using the as-obtained precursor, whereas the film prepared using the aged precursor exhibits a homogeneous structure. Electron backscatter diffraction and scanning electron microscopy analyses showed that the $Gd_2Zr_2O_7$ grains present within the regular-shaped regions are polycrystalline, whereas those present in the surrounding are epitaxial. Some polycrystalline regions ranging from several micrometers to several tens of micrometers grew across the NiW grain boundaries underneath. To understand this phenomenon, the properties of the precursors and corresponding xerogel were studied by Fourier transform infrared spectroscopy and coupled thermogravimetry/differential thermal analysis. The results showed that both the solutions mainly contain small Gd—Zr—O clusters obtained by the reaction of zirconium acetylacetonate with propionic acid during the precursor synthesis. The regular-shaped regions were probably formed by large Gd—Zr—O frameworks with a metastable structure in the solution with limited aging time. This study demonstrates the importance of the precise control of chemical reaction path to enhance the stability and homogeneity of the precursors of the CSD route.

1. Introduction

Chemical solution deposition (CSD) is a versatile technique for thin film deposition. Diverse functional oxide thin films with a well-controlled structure including ferromagnetic, superconducting, and colossal magnetoresistive materials have been successfully grown, thus achieving advanced physicochemical properties [1]. In the field of second-generation high-temperature superconductor (2G-HTS) tapes, CSD routes offer the possibility of modulating the microstructure [2] as well as fabricating high-performance products at a low cost [3], therefore contributing to both fundamental research and practical applications.

To achieve large-scale applications of 2G-HTS tapes, for example, in the fields of power transmission, fault current limiters, and rotary machines, it becomes crucial to lift a high performance/cost ratio. Among the fabrication routes developed so far, rolling-assisted biaxially textured substrates (RABiTS) combining with CSD are considered as one of the promising routes that could balance the performance and cost. Extensive studies have been conducted to better understand the processes and further increase the performance/cost ratio of the final production. Very recently, two world-leading 2G-HTS tape manufacturers working on solution-based production technology, American Superconductor (USA) and BASF (Germany), have decided to jointly develop an advanced CSD process [4], indicating a great potential of this technique for industrialization.

A CSD route has three main steps, i.e., solution synthesis, coating, and sintering. Among them, solution synthesis is a prerequisite to obtain a high-quality film. Solution chemistry is mostly related to the chemical reaction path of the precursor and thus strongly affects the microstructure, affording the final products with various properties. Effect of the precursor properties would be even more complex for those CSD routes that heavily involve environment-sensitive hydrolysis and chelation processes. For example, in the CSD processes for a YBCO film deposition, the presence and amount of fluorine in the precursor are crucial for the phase formation [5]. For oxide buffer layers, the dependence of film quality on the solution chemistry is probably not so strong because of

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the simple solution and relatively weak cation interactions (in most of the cases, one or two cations compared to at least three cations in YBCO precursors). However, solution stability is one of the most important issues in mass-production technology.

The main aim of this study is to better understand the solution aging effect on the microstructure of $Gd_2Zr_2O_7$ (denoted as GZO) films grown on textured NiW substrates. It is known that $RE_2Zr_2O_7$ family members with pyrochlore structure (RE is rare-earth element) are good candidates for buffer layers, because of (i) small lattice mismatch with either the substrate or YBCO layer (ii) excellent barrier properties against elemental diffusion during YBCO deposition at a high temperature. Several studies showed that $La_2Zr_2O_7$ [6], GZO [7], or their composition [8] served as a buffer layer for the high performance of superconducting films. Our recent studies also show that using YBCO/$Ce_{0.9}La_{0.1}O_2$/GZO/NiW architecture, a promising critical current density of 2.2 MA/cm^2 (77 K, self-field) was achieved by using an all-CSD route [9]. Compared to intensive studies on the effect of crystallization processes on texture, morphology, and porosity [10–12], the stability of $RE_2Zr_2O_7$ precursors has been rarely reported [13]. In this study, we thoroughly investigated the aging effect of GZO precursor on the film texture. The surface defects on the fully reacted GZO films were characterized by scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD) techniques. To better understand the defect formation, the precursor solutions and xerogels were analyzed by Fourier transform infrared (FTIR) spectroscopy, thermogravimetry (TG), and differential thermal analysis (DTA).

2. Experimental Section

2.1. Solution Preparation

To study the effect of precursor chemistry on the microstructure of a fully reacted GZO film, propionate-based precursor solutions were prepared following the procedure reported in the literature [14]. First, the reagents gadolinium(III) 2,4-pentadionates (Aldrich) and zirconium(IV) 2,4-pentanedionate (Aldrich) were dissolved in propionic acid (>99%, Alfa Aesar) in a flask. Second, the flask was sealed, and the reaction mixture was heated at 150 °C under magnetic stirring using a hotplate until all the reagents completely dissolved in the acid. This process took <5 h, and a light yellowish solution was obtained. This as-obtained solution of 0.4 M, i.e., $c(Gd^{3+}) = c(Zr^{4+}) = 0.2$ M, was denoted as S-A. The stability of solution S-A was found to be very high at room temperature, up to several months without any color change or precipitation. To accelerate the aging process, solution S-A was heated at 150 °C for about two weeks using a hotplate, affording a dark brown aged solution. To compensate the evaporation of solvent during the long-time heating, the total cation concentration of both the solutions was adjusted by adding a certain amount of propionic acid. The aged solution with the same concentration of 0.4 M was denoted as solution S-B. The images of the solutions are shown in Fig. 1, clearly showing the color difference.

2.2. Coating and Crystallization

(001) ⟨100⟩ orientated NiW alloy tapes (Evico GmbH) were used as the substrates. Previous studies confirmed that a "clean" interface plays an important role on the epitaxial growth of oxide films on technical substrates [12]. Therefore, the NiW substrates were annealed under a flow of 5% H_2/N_2 at 850 °C for 20 min to remove the thin oxide layer formed during the storage. Prior to coating, the substrates were also cleaned in an ultrasonic ethanol bath for 5 min and dried using compressed air. The dip coating process was carried out under ambient conditions. After immersing the substrate into the precursor, a withdrawal speed of 40 mm/min was applied. The coated films were dried in air for several minutes and directly inserted into an alumina-tube furnace for crystallization under a flow of 5% H_2/N_2 as reported previously [12,14]. Solutions S-A and S—B showed very comparable rheological properties, e.g., similar viscosity values of 1.2–1.3 mPa/s and good wettability with NiW substrates. Finally, uniformly colored GZO films with a thickness of 30 nm were obtained under these conditions. The films prepared from solutions S-A and S-B were denoted as films F-A and F-B, respectively.

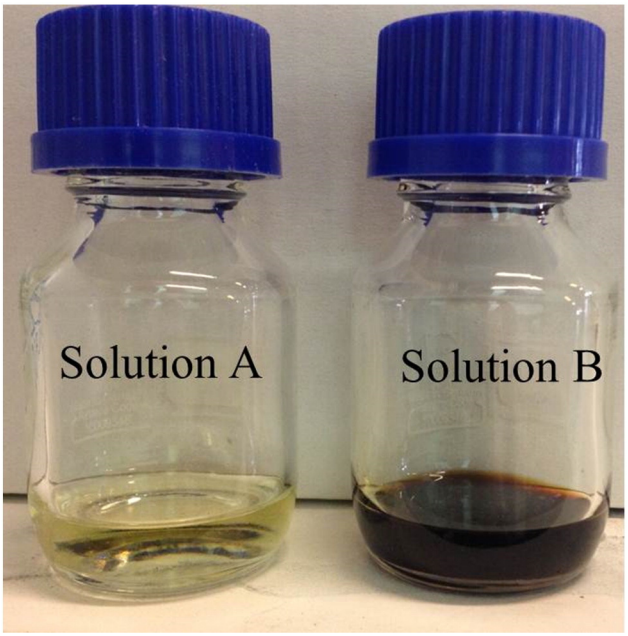

Fig. 1. Images of the as-obtained solution (solution S-A) and aged solution (solution S-B).

2.3. Characterization

The phase and texture of the fully reacted films were investigated using a four-circle diffractometer (Bruker D8) with Cu Kα radiation. EBSD measurements for local surface texture analysis were carried out using a SEM (Zeiss Supra 35) equipped with an HKL detector. The Kikuchi patterns were automatically analyzed using a data handling software package (Channel 5). The surface morphology of the films was observed by SEM using an in-lens detector.

To understand the properties of precursor, the FTIR spectra of the xerogel and precursor solutions were recorded using a Bruker Tensor 27 spectrometer. The xerogel specimens were prepared by drying the precursor at room temperature for one week. Prior to the measurements, the dried xerogel samples were ground into a fine powder. TG and DTA measurements were carried out at temperatures of up to 1200 °C using a model STA 449C instrument from Netzsch (simultaneous TG/DTA device) at a heating rate of 5 K/min. Two dynamic heating atmosphere conditions, i.e., argon and technical air, with a fixed gas flow of 40 mL/min were used. Alumina crucibles with a dimension of 6 mm in diameter and 3 mm in depth were used during the measurement. Buoyancy corrections were performed using the data recorded on empty crucibles. The mass of the powder sample was ~10 mg for all the measurements.

3. Results and Discussion

3.1. Characterization and Analysis of Surface Defects

First, a typical θ–2θ XRD scan was performed on films F-A and F-B. As shown in Fig. 2a, no secondary phase was detected on the films, and a strong c-axis texture formed as evidenced by intense GZO (004) peaks in the θ–2θ scans. Moreover, four-folded sharp peaks were obtained in the φ-scans of GZO (222) reflection. The average full width at half maximum (FWHM) values of the peaks were 7.2° and 6.6° for films F-A and