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Structural and mechanical properties of $YBaCo_4O_{7+\delta}$ thin films deposited on c-Al_2O_3 substrates by *dc* magnetron sputtering

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Abstract

High-quality $YBaCo_4O_{7+\delta}$ powders were obtained by standard solid-state reaction. The powders were pelletized and sintered at 1300 °C. The targets were subsequently coupled to a *dc* magnetron sputtering cannon using commercial silver epoxy. $YBaCo_4O_{7+\delta}$ thin films ($\sim$100 nm) were then grown on c-Al_2O_3 single-crystal substrates heated at 750, 800 and 850 °C. Microstructural analysis was carried out by means the X-ray diffraction measurements. A strong dependence of the crystalline quality of the thin films on the substrate temperature was evidenced. In turn, Young's modulus and nanohardness values of $YBaCo_4O_{7+\delta}$, both in bulk and thin film form, were determined by means of nanoindentation measurements. The values of Young's modulus and hardness obtained for $YBaCo_4O_{7+\delta}$ in bulk form were in good agreement with those encountered for thin films. Before the deposition of the films, the thermal expansion coefficients of the $YBaCo_4O_{7+\delta}$ target and the sapphire substrates were determined using a dilatometry technique. The thermal expansion coefficients of the target and the sapphire substrates ended up being very close each to other, which favors the growing of the thin films. Finally, the lattice strain, the lattice deformation stress and the deformation density energy of the thin films were also estimated from the X-ray diffraction measurements using the Williamson–Hall model. The achieved results show that the Williamson–Hall methodology is a good alternative method to estimate stress and mechanical properties of materials in thin film form.

Keywords: C. Mechanical properties; Cobaltites; Thin films; Nanoindentation

1. Introduction

In recent years, Co-based compounds have been intensively investigated due to the existence of intriguing electronic, structural and magnetic properties as well as the competition among spin states and various charge, orbital, and lattice degrees of freedom [1]. The different spin states of Co ions and the two-dimensional (2D) layered structure of the cobaltites determine decidedly the rich variety of physical properties exhibited by this class of compounds [2]. In this regard, the recently discovered cobalt-rich $YBaCo_4O_{7+\delta}$, denoted as 114, has attracted interest because of the opportunity it provides to study many of the above-mentioned phenomena in one system [3]. The crystal structure of $YBaCo_4O_{7+\delta}$ can be described in the reciprocal space of the hexagonal unit cell ($a=b=6.298$ Å, $c=10.246$ Å) [4]. Apart from the physical aspects, the technical aspects of this interesting material are likewise very attractive. The high ionic and electronic conductivity and the catalytic and electrocatalytic properties make

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these cobaltites promising materials for the development of electrochemical devices such as cathodes in solid-state fuel cells, membranes for oxygen separation, and various sensors [5]. For many applications, high-quality thin films need to be grown on crystalline substrates. The physical properties of cobaltite films are strongly dependent on the crystalline quality and the texture, which in turn depend very much on the process parameters and substrate materials. For the deposition of $YBaCo_4O_{7+\delta}$ films, commercially available *c*-axis oriented sapphire substrates (c-Al_2O_3) with lattice parameters $a = 4.765$ Å and $c = 10.298$ Å may offer reasonable conditions for a textured growth because of their hexagonal structure closely related to that of $YBaCo_4O_{7+\delta}$. For the epitaxial growth of films on large-lattice-mismatch systems, the so-called "domain epitaxial orientation relationship" has been proposed [6], where *m* lattice constants of the epilayer match with *n* of the substrate with only a small residual domain mismatch. Thus, only uniaxial locked epitaxy may also result in a high crystallinity of the films. Within the literature, only a few reports have been published on the growth and characterization of $YBaCo_4O_{7+\delta}$ films grown on crystalline substrates using physical deposition methods. For instance, Montoya et al. [7] have reported on the growth of $YBaCo_4O_{7+\delta}$ thin films on r-Al_2O_3 substrates using *dc* magnetron sputtering technique. Although some structural, electrical and magnetic properties of these films were reported in this paper, no information about their mechanical properties is to be found in the cited work. It is widely known that the technological advance in the field of materials science and engineering requires improving the growing techniques of thin films and establishing the relationship between synthesis of materials with specific characteristics and mechanical properties. As microstructure is strongly dependent on the synthesis process, it is the connecting factor between properties and synthesis conditions. Thin films can store energy and provide activation force due to the residual stress caused by the lattice and/or thermal mismatch between the growing material and the substrate. A number of applications in micro actuators, such as micropumps, microvalves, and microsensors, have been achieved based on this effect [8]. The residual stress state, which is dependent on the synthesis method, is a parameter that affects decidedly the material properties. This parameter describes macrostrains in the crystal lattice that are evident in the variation of the lattice parameter [9]. In general, the distance between the atoms constituting the lattice defines the final properties displayed by a certain material. Hence, residual stress is a key parameter determining the synthesis–property relationships. It is clear that a complete characterization of a material demands that this parameter to be not considered as independent of the microstructure. There are several methods to characterize the microstructure and residual stress of materials. One of the most common is X-ray diffraction. This technique has some advantages over others. For example, the high penetration depth in the sample allows one to test high dislocation density values without provoking irreversible damages in the specimen [10]. Therefore, X-ray diffraction is a useful method to characterize materials in terms of their microstructural properties. The microstructure and residual stress state can be evaluated from the X-ray powder diffraction patterns assuming the methodology proposed by Williamson–Hall (W–H) and Warren–Averbach [11]. The microstructure and the residual stress can then be correlated with the hardness values, which are commonly obtained using nanoindentation measurements [12].

In the present paper, the microstructural and mechanical properties of $YBaCo_4O_{7+\delta}$ thin films grown on c-Al_2O_3 substrates by *dc* magnetron sputtering are reported. X-ray diffraction and nanoindentation are used as experimental techniques to characterize the mechanical properties of the films. Microstructure and residual stress are evaluated using a methodology proposed in the Williamson–Hall model.

2. Experiment

Polycrystalline $YBaCo_4O_{7+\delta}$ was prepared by standard solid-state reaction using Y_2O_3, $BaCO_3$, and Co_3O_4 as starting reactants. Sputtering targets were fabricated by pressing the previously characterized powders into pellets and sintering them in air at 1300 °C for 20 h [13]. The planar targets were mounted on a cooper halter and the complete set was then assembled into a sputtering cannon. From these targets, $YBaCo_4O_{7+\delta}$ thin films were deposited by *dc* sputtering at a high oxygen pressure (3 mbar) onto c-Al_2O_3 substrates ($a = 4.765$ Å, $c = 10.298$ Å). The substrate temperature was varied from 750 to 850 °C. After the deposition, the chamber was flooded with oxygen at a pressure of about 200 mbar and the films were then annealed at 550 °C for 15 min. X-ray diffraction patterns in standard Brag–Brentano configuration were obtained to characterize the microstructure of the thin films. The microstructure and morphology of the films were evaluated by the field-emission scanning electron microscope (FESEM), and Atomic Force Microscopy (AFM), respectively. The thermal expansion coefficient (αL) of the $YBaCo_4O_{7+\delta}$ target and the c-Al_2O_3 substrate were measured using a Netzsch DIL 402C dilatometer. Nanoindentation analyses were performed with an IBIS Authority instrumented nanoindenter using a Berkovich-type diamond indenter. The applied charges were 5, 10, 20 and 50 mN for the target and 0.8 mN for the thin films. The Williamson–Hall model was used to evaluate the mechanical properties of both the target and the thin films. The information was extracted from the X-ray diffraction patterns by taking the peak broadening and the position of the diffraction peaks into account.

3. Results and discussion

Fig. 1(a) shows the XRD pattern of the $YBaCo_4O_{7+\delta}$ target sintered using the procedure described in the latter section. The XRD results indicate that $YBaCo_4O_{7+\delta}$ targets are single phase (within the detection limit of XRD) with hexagonal crystal structure (space group $P6_3mc$). No traces of secondary phases are observed in this plot. The lattice parameters obtained by the Rietveld refinement resulted to be $a = 6.301$ Å and $c = 10.244$ Å which are very close to those