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Investigation of Structural and Optical Properties of GDC Thin Films Deposited by Reactive Magnetron Sputtering

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The purpose of this paper was to analyze structural and optical properties of gadolinia-doped ceria (GDC, $Ce_{0.9}Gd_{0.1}O_{1.95}$) thin films. At first the ceria–gadolinia multilayer sandwich systems (4–12 layers) were deposited using reactive magnetron sputtering in the O_2/Ar gas mixtures. The films were formed with ≈ 90% ceria and ≈ 10% gadolinia. The GDC thin films deposited on Si (111) substrate were annealed at 600 ℃ for 1 h in air. The thickness of the formed GDC multilayer systems was about 600 nm. The GDC thin film microstructure was investigated by X-ray diffraction and scanning electron microscopy. The texture coefficient $T_{c(hkl)}$ of GDC films was evaluated from the X-ray diffraction patterns. The crystallite size of GDC films was estimated from the Scherrer equation. Optical properties of the annealed GDC thin films were examined using a laser ellipsometer. The results show that the number of layers has the influence on GDC thin film formation. As follows from the analysis of structural and optical properties of GDC 12 layer system annealed at 600 ℃ for one hour in air has the highest refractive index $n = 2.17$.

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1. Introduction

Ceria-based materials are of potential interest [1]. Low-temperature solid oxide fuel cells (SOFC) have attracted much attention in recent years [2]. Gadolinia-doped ceria (GDC, $Ce_{0.9}Gd_{0.1}O_{1.95}$) is considered to be one of the most promising electrolytes for SOFCs to be operated below 700 ℃ [3], primarily due to its high ionic conductivity at reduced temperatures [2]. The high operating temperature of traditional SOFC has caused many problems, such as limited materials section, high manufacturing cost, fast performance degradation of cell components, and low thermal cycling reliability [4]. Electrolyte has the greatest influence on the SOFC performance [5]. The low-temperature operation provides an economic benefit through possible replacement of some of expensive ceramic components of the cell by relatively cheaper stainless steel alternatives. It can eliminate problems caused by reaction of the electrolyte with other cell components, lower degradation problems, less thermal mismatch and interfacial losses [6].

Doped ceria oxide thin films could be prepared by the vapour processing methods: chemical vapour deposition, electrochemical vapour deposition, magnetron sputtering, plasma spray, etc. [6]. A well-developed deposition technique for preparing thin film electrolytes is sputtering [7]. Magnetron sputtering is a promising and flexible technique [8]. In this study structural and optical properties of GDC thin films prepared by reactive magnetron sputtering in the reactive O_2/Ar gas mixtures were investigated.

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2. Experimental

Gadolinia-doped ceria (thickness of all formed films was ≈ 600 nm) thin films were prepared by reactive magnetron sputtering in the reactive O_2/Ar gas mixtures. The deposition was done using two pure Ce (99.99%) and Gd (99.99%) targets in the same chamber. Gadolinia-doped ceria multilayer systems (4–12 layers) were formed. Gadolinia-doped ceria thin films were deposited by the "layer by layer" method. Firstly, $Ce_{x1}O_{y1}$ then $Gd_{x2}O_{y2}$ was deposited on the Si (111) substrate. General thickness (≈ 600 nm) of the thin films included an increasing number of $Ce_{x1}O_{y1}$ and $Gd_{x2}O_{y2}$ layers, keeping in mind, that $Ce_{x1}O_{y1}$ must be 90 at.% and $Gd_{x2}O_{y2}$ — about 10 at.%. The basic parameters of magnetron sputtering are presented in Table I.

TABLE I

The experimental conditions and process parameters.

Experimental conditions	Parameters
discharge current I [A]	0.75–1
distance between magnetron and substrate d [cm]	4
O_2 flow in the chamber F_{O2} [ml/min]	20
Ar flow in the chamber F_{Ar} [ml/min]	90
U_{Ce} [V]	240
U_{Gd} [V]	170
t [s]	360
primary pressure [Pa]	8×10^{-3}

The GDC thin films were annealed at 600 ℃ for 1 h in air. The annealing experiment was performed in the electrical heater (SNOL6.7/1300).

X-ray diffraction (XRD) studies of the GDC thin films were carried out using a θ–2θ Bragg–Brentano geometry

DRON 3.0 diffractometer with Cu K_α radiation which corresponds to an X-ray wavelength of 0.15406 nm. The samples were scanned with a 0.02° step in the 20°–100° 2θ range. The parameters such as peak position, full width at half maximum (FWHM) and intensity were extracted from all XRD diagrams using either Full Prof Suite or X-Fit software packages. The crystallite size of GDC thin films was obtained from the peak width at the mean height of X-ray diffraction using the Scherrer equation [9]. The instrumental line broadening was small compared with that of the sample line.

The XRD results were quantified by defining the texture coefficient $T_{c(hkl)}$. This factor can be calculated for each orientation using the following equation [5]:

$$T_{c(hkl)} = \frac{I_{(hkl)}/I_{0(hkl)}}{(1/N)\left[\sum_N I_{(hkl)}/I_{0(hkl)}\right]}, \tag{1}$$

where $T_{c(hkl)}$ is the texture coefficient of the *hkl* plane, $I_{(hkl)}$ is the measured intensity, $I_{0(hkl)}$ is the relative intensity of the corresponding plane given in PDF-2 data, and N is the number of reflections.

The surface and cross-section of thin films were observed by scanning electron microscopy (SEM, JEOL JSM-5900). The optical properties of the formed GDC thin films were investigated using a laser ellipsometer Gaertner L117 with He–Ne laser (λ = 632.8 nm) and the program "FilmEllipse SCI Scientific Computing International" was used to calculate the refractive index.

3. Results and discussion

In Fig. 1*a* and *b* the θ–2θ diffraction patterns of the pure Gd and Ce targets show that the crystalline structure and space group are cubic and *Ia3* for Gd_2O_3 and *Fm3m* for CeO_2. The lattice constants of Gd_2O_3 and CeO_2 thin films calculated from the XRD results are 10.811 Å and 5.4211 Å. However, it should be pointed out that the development of cubic type structure of Gd_2O_3 in CeO_2 cannot be clearly identified from XRD since both XRD patterns are nearly the same.

The preferred (111) orientation of the GDC thin films is shown in Fig. 1*c*–*e* for 4, 6 and 12 layers, respectively. Texture coefficients of all planes were calculated, Table II shows the data for the planes (111), (220), (311), and (222). From the texture coefficient the domination of crystallite orientation in the films could be described. The (111) plane has the highest value of $T_{c(hkl)}$ for 4 and 6 layers, respectively, and for 12 layers there is obtained a sudden jump of $T_{c(222)}$ value (Table II). This increase in the $T_{c(hkl)}$ value, calculated from the quasi-forbidden (222) reflection, could be the result of the increase in its structural factor, presumably induced by lattice deformation. The crystallized cubic fluorite structure of electrolyte films with a (111) preferred orientation is also believed to have the best conductivity [7].

Variation of the crystallite size of different GDC layers as a function of 2θ is presented in Fig. 2. There could be seen the decrease of crystallite size from 15.8 nm to 6.7 nm for 4 and 12 layers, respectively. Thin GDC 6÷GDC 12 layers for all crystallographic orientations are the same.

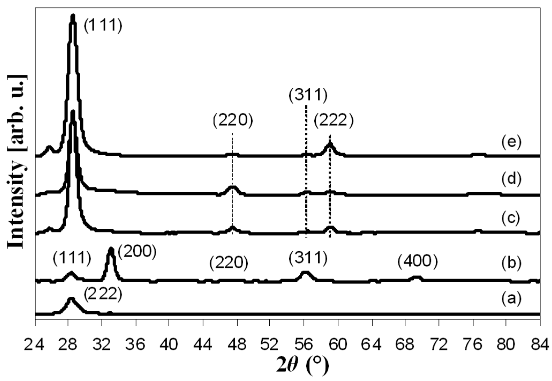

Fig. 1. X-ray θ–2θ diffraction patterns measured for (*a*) Gd_2O_3 and (*b*) CeO_2 layers obtained from pure Gd and Ce targets, respectively, (*c*) GDC 4 layers, (*d*) GDC 6 layers, (*e*) GDC 12 layers.

TABLE II

Texture coefficient $T_{c(hkl)}$ dependence on the number of layers of GDC thin films annealed at 600 °C.

Texture coefficient	$T_{c(111)}$	$T_{c(220)}$	$T_{c(311)}$	$T_{c(222)}$
4 layers	2.013	0.189	0.091	1.707
6 layers	2.016	0.467	0.193	1.324
12 layers	1.609	0.057	0.052	2.282

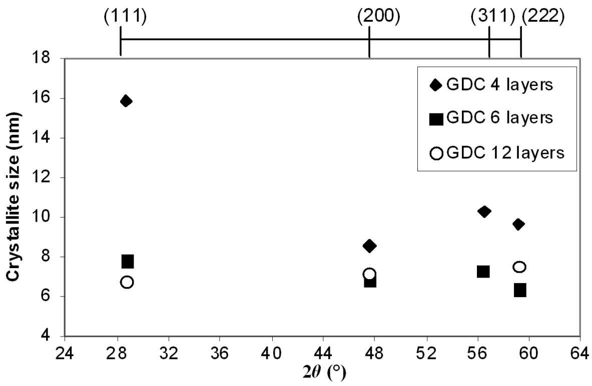

Fig. 2. Variation of the crystallite size of different GDC layers as a function of 2θ.

In Fig. 3 it is clearly identified that the refractive index n of the GDC thin films increased by increasing the number of layers when the films are annealed at 600 °C. The highest n was obtained for the 12-layer system (n = 2.17). It could be explained that increasing the number of layers, after annealing led to a denser structure. The $Ce_{x1}O_{y1}$ and $Gd_{x2}O_{y2}$ layers are very thin and can easily mix with each other. The extinction coefficient k of GDC thin films was negligible ($k \approx 0$).

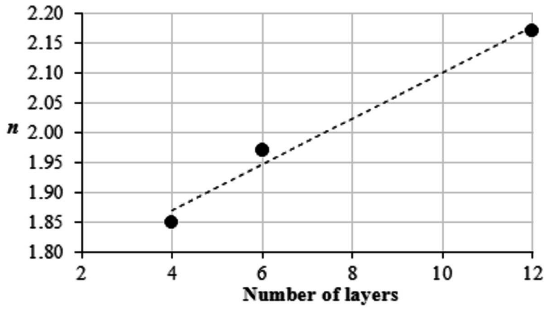

Fig. 3. Refractive index n of GDC thin films annealed at 600 °C as a function of a number of layers.

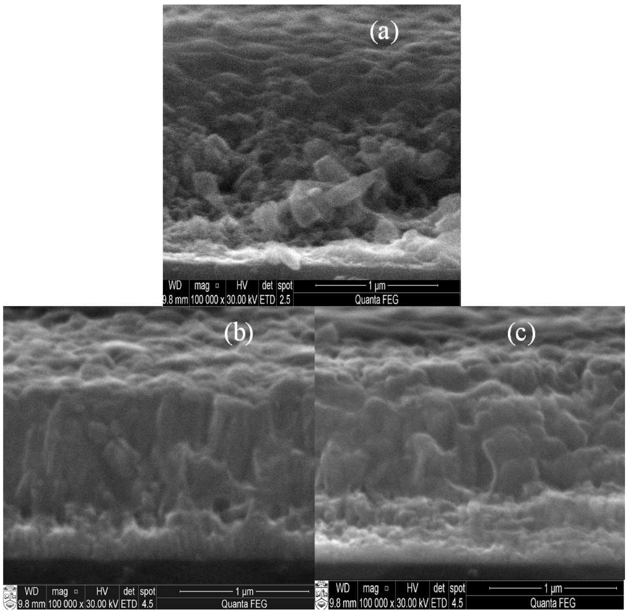

Fig. 4. Cross-sections of the GDC thin films with a different number of layers annealed at 600 °C: (a) 4 layers, (b) 6 layers, (c) 12 layers.

By reactive magnetron sputtering films were obtained with columnar structure, but after the annealing process columns disappeared and dense material was formed. Figure 4 shows the cross-section of the GDC thin films annealed at 600 °C. Part (a) shows that the layers are mixed with each other and form dense structure. In parts (b) and (c) the columnar structure with separate dense areas can be found.

4. Conclusion

This work shows that using the "layer by layer" method (reactive magnetron sputtering) for deposition, after annealing at low temperature (600 °C) the gadolinia-doped ceria thin films could be obtained applicable as SOFC electrolyte. The main results show that $Ce_{0.9}Gd_{0.1}O_{1.95}$ thin films grow with preferred (111) orientation. The electrolyte films with the (111) preferred orientation are believed to have the best conductivity. The crystallite size decreased by increasing the number of layers. The refractive index n of GDC thin films increased by the increasing number of $Ce_{x1}O_{y1}$ and $Gd_{x2}O_{y2}$ layers. The highest refractive index ($n = 2.17$) was obtained for the 12-layer GDC film system.

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