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Atomic force microscopy investigations of gadolinia doped ceria thin films prepared by pulsed laser deposition technique

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The growth of gadolinia doped ceria films with controlled surface structure for optimum device performance often presents a significant technological problem for experimental investigation. In the present investigation, gadolinium doped ceria (GDC) thin films were prepared by pulsed laser deposition (PLD) and were studied for their surface structure evolution in relation to various growth parameters. The deposition was made with gadolinia concentrations 5, 10, 15, and 20 mol % to ceria pellets. The dependence of laser energy on 10 mol % GDC thin film was studied. The effect of substrate and substrate temperature on 20 mol % GDC thin film was also investigated. The base pressure was kept at 3.5×10^{-5} mbar during all the studies. The films were characterized using atomic force microscopy (AFM). The AFM results gave a consistent picture of the evolution of GDC film surface morphologies and microstructures in terms of growth behaviour, shape, and particle distribution.

Key words: *pulsed laser deposition; atomic force microscopy; gadolinia doped ceria*

1. Introduction

CeO_2-based materials have been intensively studied as catalyst supports and promoters for heterogeneous catalytic reactions. They have found application as oxide ion-conducting materials in electrochemical devices [1]. These applications require preparation of fine powders to be used as precursors for manufacturing bulk ceramics, coatings, films, and composites [2, 3]. The doped ceria electrolytes have increased ionic conductivity compared to the conventional yttrium-stabilized zirconia (YSZ) and

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they may operate at lower temperatures (below 900 K). Various synthesis approaches using solid route, often called the "solid state reaction route," can provide a good homogeneity of the raw materials due to reagent mixing occurring at molecular level. The resulting oxide powders have a high specific surface area and, consequently, a high beneficial reactivity.

The pulsed-laser deposition (PLD) grown GDC films have been demonstrated to exhibit enhanced performance when compared to films obtained by other conventional deposition techniques. However, detailed investigations on the fundamental understanding of the growth behaviour and surface quality of these pulsed-laser deposited GDC films have not been made. Understanding the growth and morphological evolution of pulsed-laser deposited GDC films in relation to the growth conditions would improve our ability not only to explore the possible technological applications of GDC films [4, 5] but also to further tune the growth conditions to obtain films with the desired characteristics [6]. In this paper, we report on the results of our investigation focused both on understanding the growth mechanism and surface-structure evolution in pulsed-laser ablated GDC thin films. During thin-film processing, the removal of oxygen from the gadolinia doped ceria (GDC) lattice occurs when heated above a certain limiting temperature in vacuum or in a reducing atmosphere [7, 8] and this results in the formation of defects or reduced phases. The phase instability along with morphological disorder usually result in the fading or poor electrochromic/electrochemical device performance when the films are integrated in multicomponent device structures. Recently, extensive and successful efforts have been undertaken to carry out thin-film processing of GDC using PLD since it is an attractive choice for the preparation of stoichiometric and high quality metal oxide thin films for various applications [9, 10].

In the present work, the surface features of pulsed-laser deposited GDC films have been examined using atomic force microscopy (AFM) in order to understand the material characteristics on the microstructure level. The atomic force microscope is a powerful and versatile tool for measuring the surface features of thin films. The surface structure can be studied without any special preparation of the surface even for non-conducting samples. Therefore, detailed surface analysis of pulsed-laser deposited GDC films using AFM could provide guidance for the fabrication of these oxide films with controlled microstructure which is an important prerequisite for their enhanced performance in device structures. Using AFM, we have shown that the GDC films of various Gd concentration (5, 10, 15 and 20 mol %) influence the growth behaviour of the films. The size and distribution characteristics of the particles making up the films are determined by the growth parameters. An attempt has been made to establish the growth kinetics and to make a qualitative analysis of the growth mechanism.

2. Experimental

Samples of GDC were prepared from ceria and gadolinia by the conventional solid-state reaction technique. CeO_2 (99.99% pure) mixed with an appropriate quantity of Gd_2O_3 (99.99% pure) was ground with a pestle in a mortar for 18 hours. About 5 g of the powder was uniaxially pressed into pellets of 20 mm in diameter and 6 mm thick at 4 tons/cm^2. These pellets were sintered at 1823 K for 6 h in air [11]. The densities of the sintered specimens were determined by the Archimedes method using dibutylthalate as the medium. All the samples used in the present study had the densities of about 90% of the theoretical value. The target was examined with X-ray diffraction and confirmed for its composition and structure before being put into the chamber for laser ablation to produce GDC thin films [4].

Thin films of GDC were prepared by varying the concentration (5, 10,15, and 20 mol %) of gadolinia, the 10 mol % GDC thin films were prepared by varying the laser energy, and finally the 20 mol % GDC thin films were prepared varying the substrates and their temperatures. A KrF excimer laser (Compex 205 from Lambda Physik) with the wavelength of 248 nm was used to ablate the GDC target. The UV laser beam focused by the lens passed through a quartz window to scan the target surface. The angle between the incident laser beam and the laser beam normal to the target surface was 45°. The energy of the laser pulse varied from 200 mJ to 600 mJ and the pulse repetition rate was set at 10 Hz. During the ablation, the target was rotated at the rate of six rotations per minute to avoid the depletion of the material at the same spot continuously and to obtain uniform thin films. Well-cleaned Si (100), and $LaAlO_3$ (100) substrates were employed for the deposition of GDC thin films. The substrates were heated and maintained at a constant temperature using a thermocouple and temperature controller. The target to the substrate distance was 4.5 cm.

The deposition chamber was emptied to a base pressure of 3×10^{-5} mbar prior to film deposition. For reactive deposition, pure oxygen gas was introduced (using flow controller) into the chamber during deposition. The thickness of all the pulsed-laser deposited GDC thin films in the present investigation was about 0.3 μm. The thickness of the film was measured using a Dektak-3010 surface profilometer. An atomic force microscope (DFM mode using SPA400, Seiko Instruments Inc) was used to study the surface morphology of GDC thin films in a tapping mode of operation.

3. Results and discussion

3.1. GDC films with different dopant concentrations

To study the influence of dopant concentration on the microstructure of GDC films, the films with various dopant concentrations (5, 10, 15, and 20 mol %) were examined. Figure 1 represents AFM 3D microstructure of GDC films deposited on Si (100) substrates at 873 K, 0.2 mbar oxygen partial pressure. The film was composed of spherical particles varying in size from 63.1 to ca. 100 nm. The root mean square value of the surface roughness (rms roughness) calculated from the AFM images, increases with the increasing dopant concentration (from 5 to 20 mol %) from 1.92 to 9.78 nm. The results have been shown in Table 1.

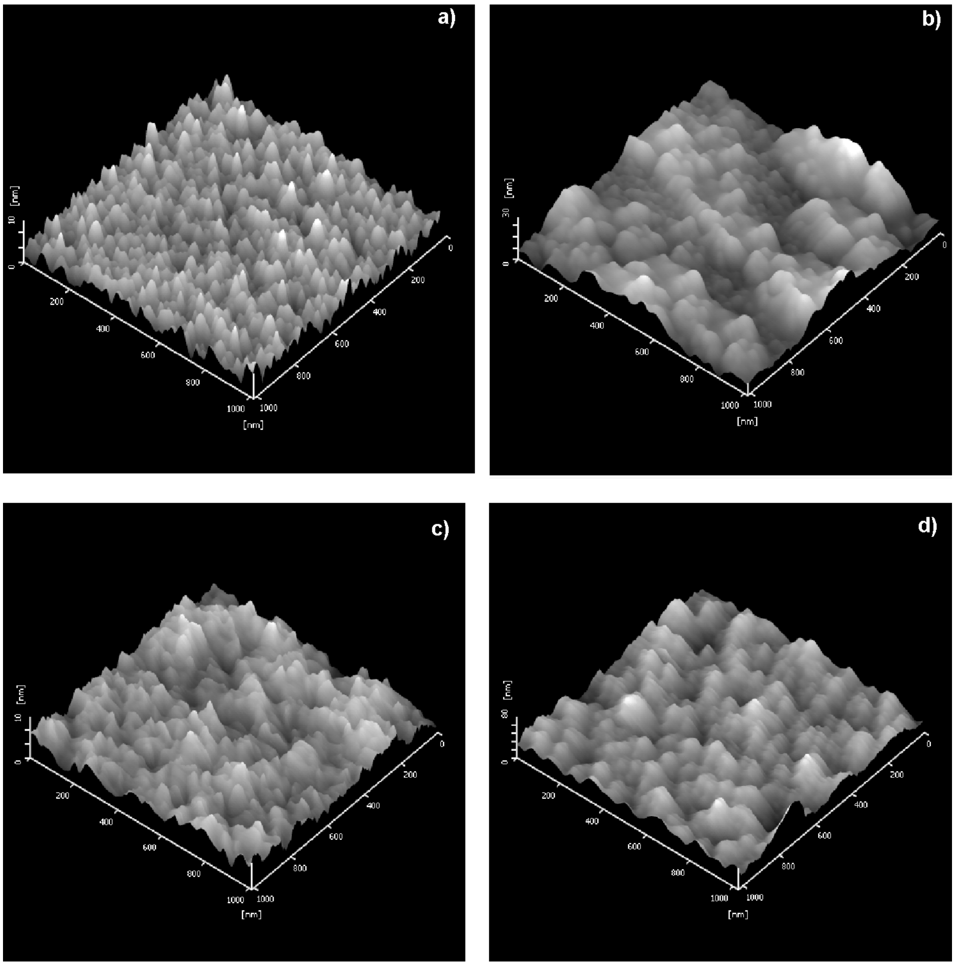

Fig. 1. 3D AFM images of GDC thin films with various dopant concentrations prepared on Si (100) at 873 K, 0.2 mbar: a) 5 mol % GDC, b) 10 mol % GDC, c) 15 mol % GDC, d) 20 mol % GDC

Table 1. The RMS roughness and mean diameter of grains of GDC thin films coated on Si (100) at 873 K and oxygen partial pressure of 0.2 mbar

Sample	RMS roughness [nm]	Mean diameter of grains [nm]
GDC – 5 mol % gadolinia	1.92	63.1
GDC – 10 mol % gadolinia	3.59	103.1
GDC – 15 mol % gadolinia	4.98	100.9
GDC – 20 mol % gadolinia	9.78	100.6

The increase in roughness may be due to the different kinetics of the dopant atoms and the host atoms on the film surface at a particular temperature. Though all the films were deposited under identical conditions at 873 K, there seems to be a significant modification in their surface topographies. It is believed that the increasing content of Gd has been found to increase the crystallite size and hence in the increase in the roughness of the films.

3.2. 10 mol % gadolinia doped ceria films prepared at various laser energies

The AFM images of the 10 mol % GDC films prepared at various laser energies from 200 to 600 mJ/pulse at 873 K are shown in Fig. 2. At low energies, the grains are distributed uniformly, their size is small, and the film seems to be smooth. As the energy increases, the grain size and roughness also increase (Table 2).

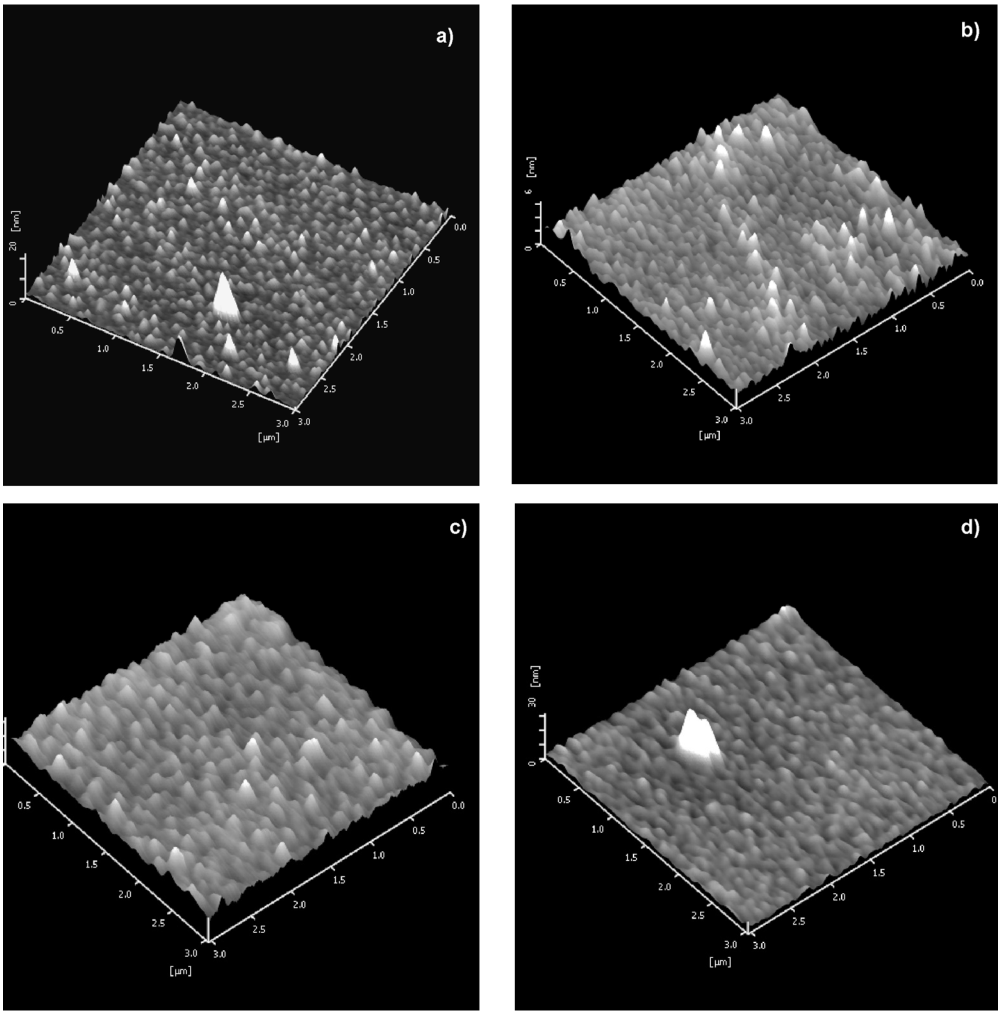

Fig. 2. 3D AFM images of GDC thin films with various laser energies prepared on Si (100) at 873 K: a) 200 mJ, b) 400 mJ, c) 500 mJ, d) 600 mJ

Table 2. The RMS roughness and mean diameter of grains of 10 mol % GDC thin films coated on Si (100) at 873K

Sample	RMS roughness [nm]	Mean diameter of grains [nm]
200 mJ	0.18	22.1
400 mJ	0.57	46.2
500 mJ	0.56	66.6
600 mJ	1.73	162.4

It is evident from Figs. 2a, b that the increase in grain growth with increasing laser energy is due to increased ablation rate of the target by incident laser energy which deposits larger amounts of ablated species on the substrate. Though AFM shows an increased grain growth with increasing laser energy, it is seen that each grain comprises several small crystallites appearing as grains on the surfaces of the films shown in Figs. 2c, d.

3.3. Effect of substrate and substrate temperature on 20 mol % GDC films

The AFM results of 20 mol % GDC thin films deposited on various single crystal substrate materials as a function of substrate temperature showed interesting features. The AFM images of GDC thin films were grown on Si (100) and $LaAlO_3$ (100) substrates, respectively. It can be seen in the images that the 20 mol % GDC thin films deposited on all substrate materials have finer microstructures with nano-sized grains spreading on the substrate surfaces uniformly [12, 13].

Another characteristic feature revealed in the present study is the change in the surface morphology of GDC thin films with increasing substrate temperature. Interestingly, it was also noticed that the surface morphological changes are different for 20 mol % GDC thin films grown on various substrate materials. The grain size of 20 mol % GDC thin films increased with the increasing substrate temperature. However, the shape, as well as the arrangement of the grains, were found to be different. It seems that the influence of substrate material characteristics is coming into play to show the effect with the increasing temperature [14, 15]. Figure 3 shows the AFM micrographs of laser-ablated 20 mol % GDC thin films grown on Si (100) (Figs. 3a, c) and $LaAlO_3$ (100) (Figs. 3b, d), at 873 and 973 K. The films grown at 873 K on both substrates showed mostly a cauliflower-like structure. This morphology shown in 2D images indicates several particles embedded in each grain. On the other hand, the films grown on $LaAlO_3$ (100) showed coarsened globular particles instead of a cauliflower-like structure at 973 K. It appears that the characteristics of the substrate material also influence the growth morphology of the deposited thin films.

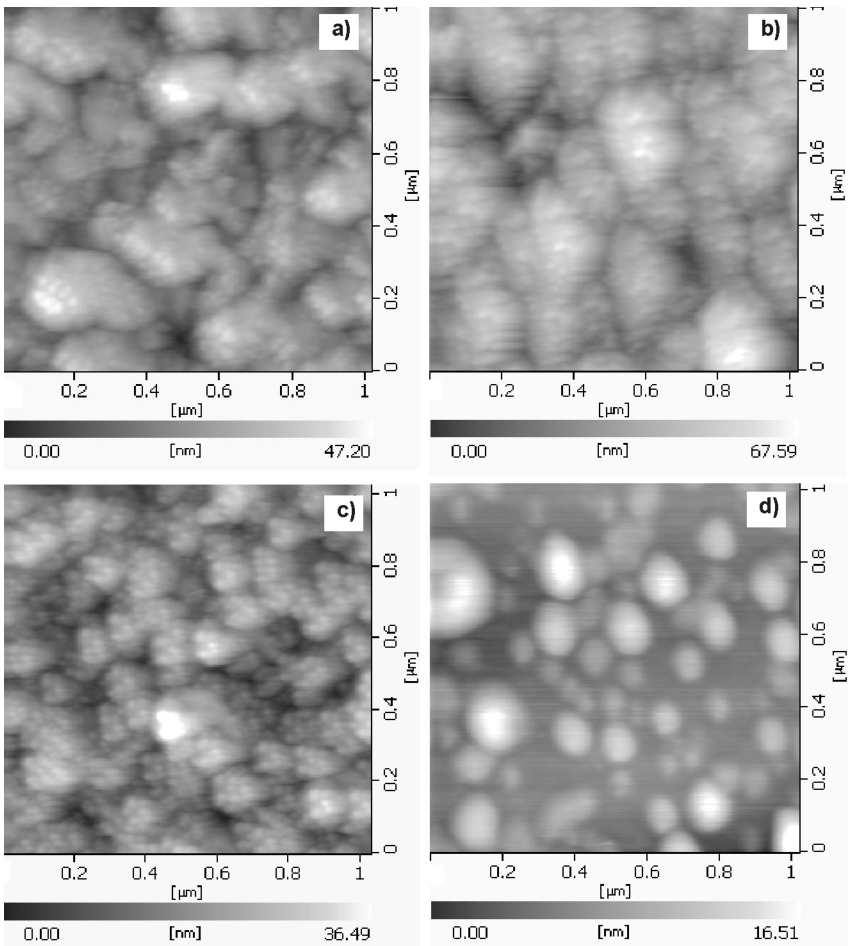

Fig. 3. 2D AFM images of 20 mol % GDC coated on: a) Si (100) at 873 K, b) $LaAlO_3$ (100) at 873 K, c) Si (100) at 973 K, d) $LaAlO_3$ (100) at 973 K

4. Conclusions

Thin films with various dopant concentrations were fabricated and examined using the atomic force microscopy (AFM). For the thin film deposited on Si (100) substrate at 873 K and 0.2 mbar of oxygen partial pressure, the RMS value of roughness increased with the increasing dopant concentration. The increase in roughness may be related to various kinetics of dopant and host atoms on the film surface at a particular energy and temperature.

For the 10 mol % GDC films prepared at various laser energies, at low energy the grain size was small and the film was smooth. With the increase of energy, grain size and roughness increased, which may be attributed to the increased ablation rate of the target with the increasing laser energy.

20 mol % GDC films deposited on Si (100) and $LaAlO_3$ (100) substrates have finer microstructure with nano-sized grains. The films grown at 873 K on both substrates showed mostly a cauliflower-like structure. On the other hand, the films grown on $LaAlO_3$ (100) showed coarsened globular particles instead of a cauliflower-like structure at 973 K. It appears that the characteristics of the substrate material also influence the growth morphology of the deposited thin films.

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