Preparation, Micro structural characterization and Optical characterization of pure and Gd-doped ceria thin films

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Abstract- The growth of Gadolinium doped ceria thin films with controlled surface structure for device applications presents a significant problem for experimental investigation. In the present study pure Cerium oxide and gadolinium doped cerium oxide thin films were prepared by pulsed laser deposition [PLD] and were studied for their surface structure evaluation in relation to the optimized operating conditions during the stage of film preparation. The deposition was made with gadolinium concentration of 10mole% to ceria pellets. The films were deposited on quartz substrate in the presence of oxygen partial pressure of $1.5X10^{-3}$torr using KrF Excimer laser with laser energy 220mJ at a substrate temperature of 700^0 C. The effect of annealing temperature on undoped cerium oxide and 10mole% GDC thin film was investigated. The film thickness was measured by using AMBIOS make XP-1 stylus profiler. As prepared and annealed thin films were characterized for crystallinity, particle size and orientation by using G.I.XRD. 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 surface roughness, grain distribution and mean grain size. The optical transmittance spectra was used to determine the optical constants such as optical band gap, refractive index of as prepared and annealed thin films.

Index Terms- Cerium oxide, micro structure, optical band gap, Pulsed Laser Deposition, refractive index, substrate, surface roughness, thin film.

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1 Introduction

Cerium oxide and Gadolinium doped cerium oxide thin films have been grabbing great interest in technological applications. Due to high refractive index , absorption of UV radiation, transparency in the visible and near-IR region which makes Cerium oxide thin films as an ideal UV blocker and excellent replacement for titanium oxide and zinc oxide in sunscreens[1],[2],[3],[4],[5].Cerium oxide plays an important role in electro chromic devices[6], as substrate for high temperature superconductor[7], Silicon-on-insulator[SOI]structure[8-9],miniatured capacitors[10],[11], counter electrode in smart windows due to its high transparency[12],[13]. Various techniques have been so far employed to prepare cerium oxide thin films such as sol gel method[14],Sputtering[15],Electron Beam evaporation[16],Metal organic chemical Vapor deposition[17],Atomic layer deposition[18],Spray Pyrolysis [19] and Pulsed Laser Deposition[PLD][20],[21],[22],[23]. Pulsed Laser Deposition is the best of all afore said techniques due to its sample uniformity, good stochiometry and also free from contamination during the deposition process. It is the most effective method to prepare extremely pure film. This method can be successfully adopted to prepare multi component material that is difficult to process in to thin film form by any other method. Cerium oxide is an electrical insulator with the fluorite structure and a lattice constant of 0.539nm. However ionic conductivity can be improved by an appropriate doping. It was reported in bulk form that the conductivity of ceria can be remarkably enhanced by increasing the concentration of oxygen vacancies after doping with Gadolinium at fixed doping concentrations. Among the rare-earth doped ceria, the radius of Gd dopant ion is the close to that of the host cation[24]. Hence, great attention has been focused on the doping of ceria by Gd to bring an improvement in its structural, morphological and optical properties.

2 Experimental Procedures

Cerium ammonium nitrate $Ce(NH_4)_2(NO_3)_6$ and Gadolinium nitrate $Gd(NO_3)_3$,99.99% were used as starting precursors and citric acid, ethylene glycol were selected for the polymerization treatment. Nitrates were dissolved in de-ionized water separately and then the solutions were mixed in beaker. Citric acid was dissolved in de-ionized water and then added to the cation solution. The molar ratio of total nitrates: citric

acid and ethylene glycol: citric acid was taken as 2:1 and 4:1 respectively. After homogenization of this solution, temperature was raised to 80°C and the solution was kept for 6 hours at this temperature on magnetic stirrer to remove additional water. The obtained gel was cooled down to room temperature. Later the compound was dried at 120°C for 24 hours. Finally the prepared powder was Calcinated at 1400°C for 8 hours. The sol gel prepared compound $Gd_{0.1}Ce_{0.9}O_{1.95}$(10GDC) was made into a pellet with 20mm diameter and 5mm thickness at a pressure of 3tonns/cm² by using hydraulic Pelletizer. The prepared pellet was again sintered at 1400°C for 8hours. Block diagram of Pulsed Laser Deposition evaporation process is shown in figure1.The laser ablation was carried out with 10GDC pellet.

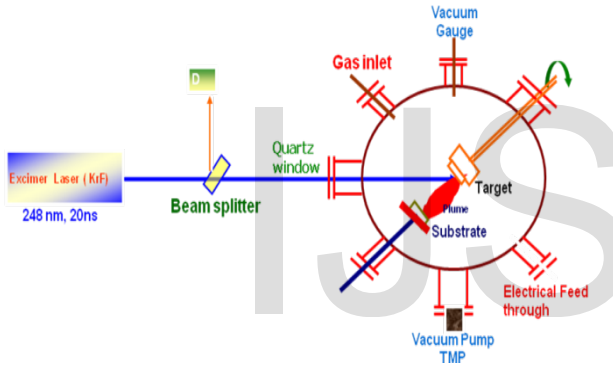

Fig.1.Block diagram of PLD evaporation process

Substrate	: Quartz plate
Laser	: KrF Excimer
Wavelength	: 248nm
Pulse repetition rate	: 10Hz
Oxygen partial pressure	: $1.5*10^{-3}$torr
Source- substrate distance	: 4cm
Substrate Temperature	: 700°C
Laser Energy	: 220mJ
Deposition time	: 30minutes

Table 1 Typical deposition parameters for PLD

In PLD the laser beam is generated outside the chamber. Also the optical instruments like lenses, mirrors and apertures, whose objective is to guide and focus the laser beam, are placed before the port of the deposition chamber. In the chamber the laser beam is directed towards the target. The absorption of the laser radiation is followed by breaking of chemical bonds in the target material and ablation of atoms, ions, electrons, molecules, atomic clusters and even bigger particles. These evaporated species form a plasma plume, which expands in the vacuum and flows towards the substrate to form the deposit. Deposition parameters are shown in the table1.

3. Results and Discussion

3.1. Thickness measurement

After deposition, thickness of the Gadolinium doped cerium oxide ($Gd_{0.1}Ce_{0.9}O_{1.95}$-10GDC) thin film has been measured by using Taly-step measurement technique. Taly–step is the stylus instrument for thickness measurement of thin film deposits having a range of applications in micro-topography and metallurgical research. The stylus is traversed over the film surface shown in figure2. A step on the substrate while deposition, there is some part on the substrate where no deposition has taken place. The stylus moving over the film, when comes to this region experiences the change or difference in heights. Vertical movement of the stylus is amplified electronically and recorded as graphical representation of the differences in level between the surface of the substrate and the deposit. Gadolinium doped Cerium oxide film thickness was found to be around400nm.

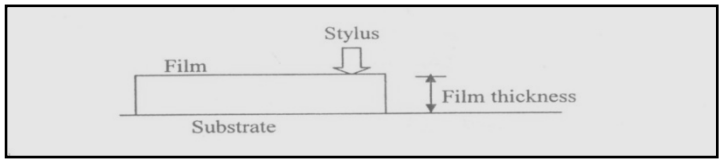

Fig.2 Taly-Step- profiler

3.2. G.I.XRD

The crystal structure of the films were investigated by G.I X-ray diffraction system and it was performed in a LiF monochromator with 1.54A°wavelength in the range of 20° to 60° with 1°/min scanning speed. Using XRD data the crystallite size of the films was estimated for preferred orientation (111) with the help of Debye Sherrer's formula. X-ray diffraction pattern of as prepared and annealed thin films are shown in the figure 3.

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$$crystallite\ size(d) = \frac{0.94\lambda}{\beta \cos\theta}$$

Where λ is the X-ray wavelength (1.54 Å), β is FWHM and θ is the diffraction angle of XRD peak.

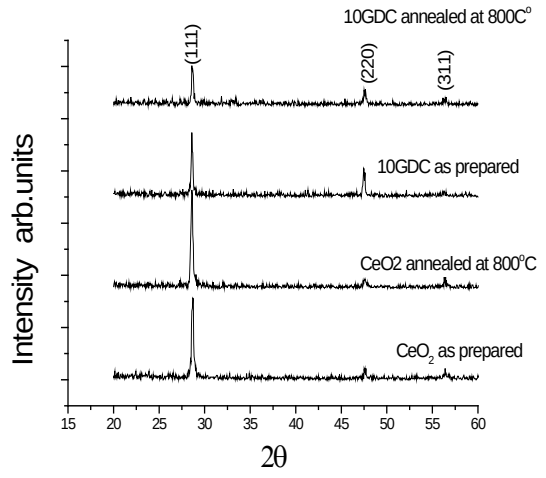

Fig.3 XRD patterns of CeO_2 and 10GDC thin films

Table: 2 crystallite size of the CeO_2 and 10GDC thin films

S.No	Sample name	Crystallite size(nm)
1	CeO_2 as prepared	30.148
2	10GDC as prepared	33.320
3	CeO_2 annealed at 800°C	34.432
4	10GDC annealed at 800°C	34.669

All the XRD patterns of the thin films indicate the polycrystalline nature. The crystallinity of the films is found to increase after heat treatment in pure ceria. Due to annealing the increase in intensity and sharpness in the XRD peaks was observed in pure ceria thin films. Crystallite size is increased from undoped cerium oxide thin films to Gadolinium doped cerium oxide thin film. Crystallite size was increased with annealing temperature. This can be attributed to increased mobility of adatoms and coalescence of small crystallite to form larger grain[25].Lattice spacing has been calculated by using Bragg's equation i.e $2d\sin\theta = n\lambda$. Calculated lattice constant is in well agreement with JCPDF data.(81-0792),(75-0161)for Cerium oxide thin film and 10GDC thin film respectively. Calculated d spacing and lattice constant values are shown in the table 3.

Table 3. d-spacing and lattice constant values of CeO_2 and 10GDC thin films

sample	(hkl)	d-spacing(nm)			Lattice constant(nm)		
		prepared	Annealed at 800°C	JCPDF	prepared	Annealed at 800°C	JCPDF
CeO_2	(111)	0.310	0.311	0.312	0.538	0.539	0.541
	(220)	0.190	0.190	0.191	0.539	0.539	
	(311)	0.162	0.162	0.163	0.540	0.539	
10GDC	(111)	0.311	0.311	0.312	0.539	0.539	0.541
	(220)	0.191	0.190	0.191	0.541	0.539	
	(311)	0.163	0.162	0.163	0.541	0.539	

3.2 Atomic force micro scopy:

Cerium oxide thin film and 10GDC thin film surface morphology characterization was carried out by using atomic force microscopy (AFM). AFM images of the films were taken in the tapping mode. The root mean square (RMS) roughness, average roughness and average height of columns are obtained from the AFM images. AFM images are shown the figure 4 and figure 5. Due to the increase in crystallite size the RMS roughness is found to decrease. It was found that RMS roughness is decreased with the doping concentration of Gadolinium in cerium oxide.

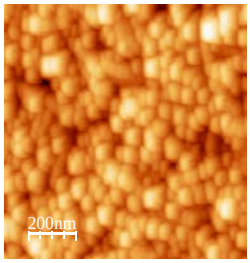

Figure 4(a)

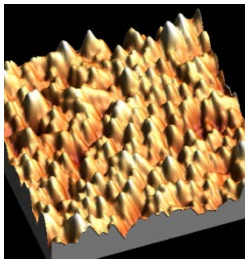

Figure 4(b)

Fig. 4(a), 4(b) 2dimensional &3 dimensional AFM images of cerium oxide thin film as prepared

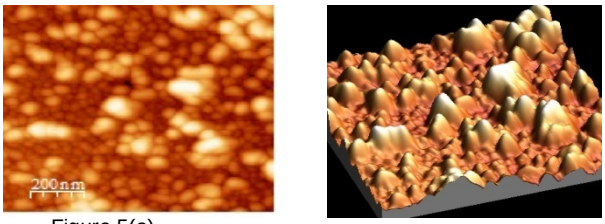

Figure 5(a)

Figure 5(b)

Fig. 5(a), 5(b) 2dimensional &3 dimensional AFM images of cerium oxide thin film annealed at 800°C

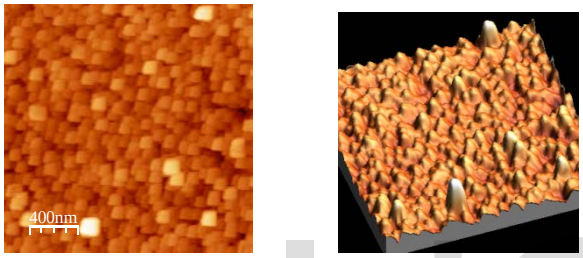

Figure 6(a) **Figure 6(b)**

Fig. 6(a), 6(b) 2dimensional &3 dimensional AFM images of 10GDC thin film as prepared

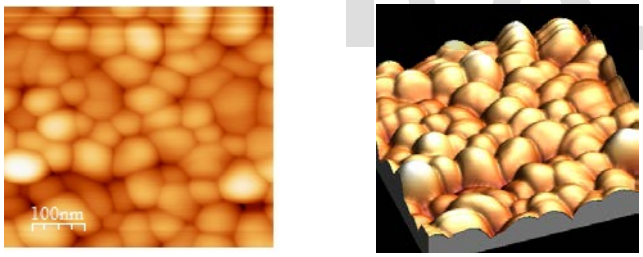

Figure 7(a) **Figure 7(b)**

Fig. 7(a), 7(b) 2dimensional &3 dimensional AFM images of 10GDC thin film annealed at 800°C

Table 4.Surface morphology of CeO_2and10GDC thin film

S.No	Description	CeO_2 thin films	
		As prepared	Annealed at 800°C
1	Average Roughness (nm)	9.59	5.32
2	RMS roughness(nm)	12.16	6.64
3	Average height of columns(nm)	48.37	15.71

S.No	Description	10GDC thin films	
		As prepared	Annealed at 800°C
1	Average Roughness (nm)	3.02	1.69
2	RMS roughness(nm)	4.14	2.18
3	Average height of columns(nm)	15.38	8.59

3.3 Optical Properties of Cerium oxide thin films

Undoped and Gd doped Cerium oxide thin film was studied by optical transmission spectroscopy to determine the optical band gap, extinction coefficient, refractive index and absorption coefficient. The transmission spectra were attained at room temperature with U.V.visible spectro photometer. The results show that the calculated data were well matched with the earlier reported work. Optical band gap of cerium oxide thin films was calculated from the analysis of the absorption spectra with following the formula [23]. Calculated optical band gap values are tabulated in table5.

$$\alpha h\upsilon = A(h\upsilon - E_g)^m$$

Where α = Absorption Coefficient, h=Plank's constant, υ=frequency of incidence light, E_g=Optical Band gap of material and m = factor affecting the direct/indirect transitions of electrons from the valence band to the conduction band. (m=2 for direct transition and ½ for indirect transition).

Figure 8(a) & 8(b) shows direct absorption of as prepared and annealed cerium oxide thin film and 10GDC thin film as a function of photon energy. Optical band gap values are shown in the following table (6). As it is seen from table (5) that there will be an enhancement in optical band gap due

to the Gd doping. The band gap found to decrease with annealing in pure and Gd doped ceria. This can be attributed due to Gd^{+3} has a half filled 4f orbital and exciting an electron from or to a Gd^{+3} ion involves breaking the stabilization provided by the maximum number of parallel spins and the excited electrons are more likely to be accommodated in the empty Ce 4f orbitals[26].

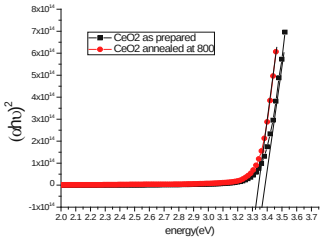

Fig.8(a)

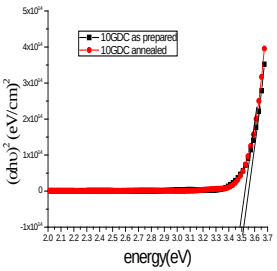

Fig.8(b)

Tauc plot for the determination of optical band gap of CeO_2 and 10GDC thin films

Refractive index of the thin films can be calculated by using the following formula

$$\left(\frac{n^2-1}{n^2+2}\right) = 1 - \sqrt{\frac{E_{opt}}{20}}$$

Where "n" is refractive index of the material and E_{opt} is the optical band gap.

Table 5.optical band gap and refractive index of CeO_2and10GDC thin films

S.No	Name of the sample	Optical band gap in eV	Refractive index(n)
1	CeO_2 thin film as prepared	3.36	2.30
2	CeO_2 thin film annealed at 800°C	3.19	2.34
3	10 GDC thin film as prepared	3.51	2.71
4	10GDC thin film annealed at 800°C	3.48	2.78

From table(5) it is noticed that refractive index found to increase with annealing temperature in pure and Gd doped ceria thin films. It could be explained that after annealing these films led to denser structure.

4. Conclusions

In the present work we have deposited Cerium Oxide thin films and 10GDC thin films by using Pulsed Laser Deposition technique on quartz substrate. Good stochiometry thin films were obtained and characterized by G.I XRD. It was found that deposited thin films are poly crystalline in nature with 400nm thickness. Deposited films are annealed at 800°C for two hours to enhance micro structural properties. It was found that crystallite size increased with annealing temperature. The atomic force micro scopy study reveals the surface properties of deposited thin films. It was observed that Average roughness, RMS roughness and Average height of columns decreased with Gadolinium doping and with annealing. Optical band gap and refractive index of the thin films were calculated from the transmittance spectra.

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