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OPTICAL PROPERTIES OF NANOSTRUCTURED CERIUM OXIDE THIN FILMS BY PULSED LASER DEPOSITION

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Abstract- *Cerium oxide (CeO_2) thin films have been prepared by using Pulsed laser deposition (PLD) technique onto the quartz substrate at a pressure of about pO_2– $2x10^{-3}$ mbar. The films were characterized using X-ray diffraction and UV-Visible spectroscopy techniques. The optical properties of cerium oxide films were studied in the wavelength range of 190 – 900 nm. The film was highly transparent in the visible region. It is also observed that the film has low reflectance in the ultra-violet region. The optical band gap of the film is determined and is found to decrease with the increase of film thickness. The X-ray diffraction of the film showed that the film is overcoming its amorphous nature to crystalline.*

Keywords: On axis Pulsed laser deposition, X-ray diffraction, amorphous nature

I. Introduction

The recent surge of activity in the wide band gap semiconductors has arisen from the need for optical materials, especially emitters, which are active in the blue and UV wavelength. The extensive research activities carried out on material to realize optical devices because of its high refractive index and good transmittance in the visible spectrum.

CeO_2, revealed its potential applications in optoelectronics. Cerium oxide (ceria) films have received considerable interest because of their high transparency in the visible and near IR region and electro-optical performance [1-4]. Rare earth oxides are potentially useful materials for various optical and electronic applications (e.g. optical filters, capacitors). CeO_2 is an interesting.

In the present study thin CeO_2 films have been deposited on a quartz substrate at room temperature, giving substrate heating at temperatures of 303, 523, and 923 K and the oxygen partial pressure 2x 10^{-3} mbar was introduced at $8x10^{-6}$ mbar of vacuum, using pulsed laser ablation technique. If the back ground oxygen pressure exceeds this value, the quality of the film may deteriorate owing to the enhanced collision of laser plume species with background oxygen atoms. In this work the structural and optical characteristics of CeO_2 thin films prepared using PLD. This is a useful physical vapor deposition technique to deposit materials with high melting points. Various characterization tools have been employed to rationalize the significance of this work. Structure identification of the films has been made by X-ray diffraction technique. Scanning electron microscopy has been employed to analyze the surface morphology of the samples. Linear optical studies include UV-VIS absorption spectroscopy. An attempt has also been made to find out the thickness of the films. The particular ability of laser deposition to grow films in reactive environments (like oxygen), makes it well suitable for applications.

2. Experimental Details

The deposition of the films is carried out inside a multi-port stainless steel vacuum chamber equipped with a gas inlet, a rotating multi-target and a substrate holder which can be heated up to 1073 K. The irradiations were performed using a Q-switched Nd:YAG laser (Quanta–Ray INDI–Series, Spectra Physics) with 90 mJ of laser energy at frequency doubled 532 nm radiation with pulse width 8ns and repetition frequency 10 Hz. CeO_2 (Merck, purity 99.995%) powder is grinded well in an agate mortar for 2 h, pressed into 11mm diameter and 3mm thickness pellet at 1.5 ton and then sintered at 1350 8C for 9 hour in air. Sintered CeO_2 pellets are used for ablation on quartz substrates. Before irradiations, the deposition chamber is evacuated down to a base pressure of $\sim 10^{-6}$ mbar. The energy density of the laser beam at the target surface was maintained at 1 J/cm^2. The laser radiation is impinging on the target at 458 with respect to the normal. The depositions of the films are done on quartz substrates kept at an on-axis distance of 65 mm. The target is rotated with constant speed during

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ablation to avoid pitting of target at any given spot and to obtain uniform thin films. The experimental details are shown in the table 1 for convenience.

Each step in PLD may influence the quality of the films. The first and foremost one is the substrate cleaning. The substrates were cleaned well with the soap solution and the quartz substrates were put in to the dilute HNO_3 and $K_2Cr_2O_7$ solution for more than one hour to completely clean the soap foams. Then the quartz substrates are washed with acetone and heated for one hour.

Table 1 shows the deposition conditions of the present work

Laser	Nd:YAG (1064)
Target	Sintered CeO_2
Substrate	Quartz plate
Target – Substrate distance	65mm
Repetition frequency	10Hz
Deposition time	20 minutes
Laser energy	90mJ
Substrate temperature	303,525.925K (A, B, C)
Oxygen partial pressure	2x 10^{-3} m bar

The targets were initially prepared by taking pure CeO_2 powder and the pellets were made. It is sintered at 900 K for nearly 5 hours. The pellets are mounted on the target holder, one at a time, inside the vacuum chamber of the pulsed laser deposition unit. Substrates are placed opposite to the target to substrate distance of 65 mm. The substrates and targets were parallel. The CeO_2 thin films were deposited on the quartz substrate using Nd:YAG laser. The characteristic of the used deposition system were a fixed laser beam, with a size of 8ns and the laser beam hits the target at an angle of 45°.

3. Results and discussions

To characterize each deposited phase, X-ray diffraction, scanning electron microscopy and energy dispersive spectroscopy and UV-Visible spectroscopy were performed and correlated.

XRD Analysis

X-ray diffractograms of the as-deposited films A, B and C are shown in Fig. 2. The constituent phase and texture of the films were identified by a powder X-ray diffract meter X'pert pro PANalytical (formerly Philips), equipped with CuKα radiation operated at 40KV-30 mA. The wavelength of Cu Kα is 1.5405 Å. A careful profile analysis of the Bragg peak intensities was performed to determine the evolution of preferred orientation of crystal sizes in the as prepared thin films. The Fig. 1 shows the XRD patterns of CeO_2 powder used for preparing the target material and is indexed according to ASTM data card No.04-0593. CeO_2 has a cubic fluorite structure, with space group *Fm*3*m* (225), and its lattice constant ao=0.541 nm. This implies an fcc lattice of the (Ce) with oxygen in all tetrahedral sites, forming a simple cubic array of oxygen. The XRD patterns of the as deposited films, CeO_2 phase should be either amorphous (no XRD Bragg peaks present in the diffraction patterns) or in a nanostructured state. Because of very weak crystal growth rate[5].

All the XRD patterns show a broad hump like feature around $2\theta = 30^{\circ}$ which can be due to the amorphous nature of the substrate or the nanocrystalline nature of the films [6]. Analysis of XRD pattern suggests that, the microstructural evolution and transformation kinetics from amorphous to crystalline phase is dependent on the substrate temperature. The as-deposited (303 K) A film is amorphous in nature whereas as-deposited (523 K) B and film is quasi-crystalline and the as- deposited (923 K) C film is polycrystalline in nature. Increase of substrate temperature enhances kinetic energy and hence the mobility of the surface species. This can be the reason for improved crystallinity of the films deposited at higher substrate temperature.

The XRD patterns of as-deposited B and C films show a less intense peak at (1 1 1) lattice reflection plane. Many of the reports show that the intensity and orientation of the XRD peaks corresponding to nanostructured films can vary widely from that of the bulk material. This is because the preferred orientation of crystalline growth which strongly depends on the deposition conditions of the films. The film C shows less crystalline even at high substrate temperatures due to defects and lack of enough kinetic energy and mobility of the grains to get oriented at respective planes.

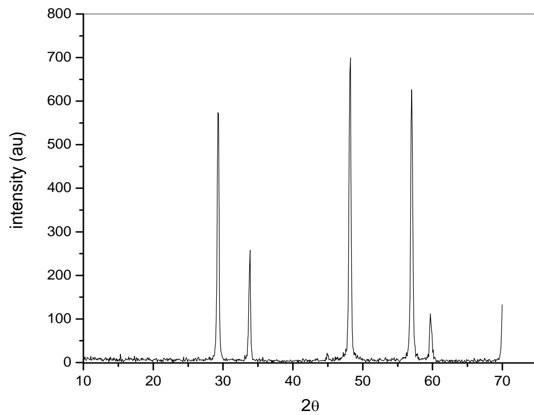

Fig. 1 Diffraction patterns of pure CeO_2 powder

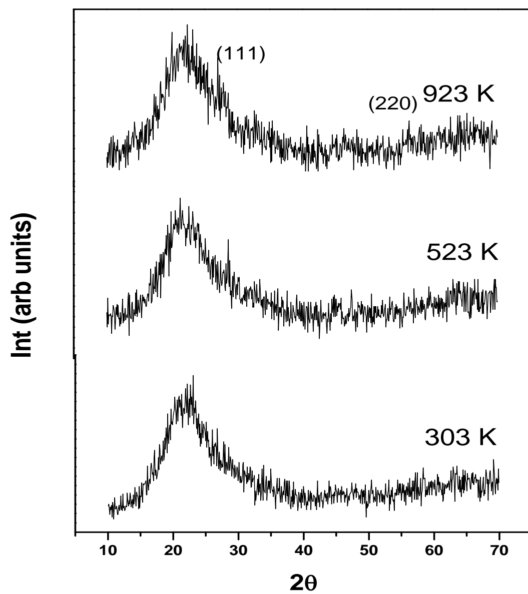

Fig. 2 The X-ray diffractograms of the CeO_2 thin films prepared at different substrate temperature like at 303, 523 and 923 K films under an oxygen partial pressure of 2x 10-3 m bar.

From the Fig. 2, the film deposited at 523 and 923 K shows the peaks corresponding (111) and (220) peaks of weak intensity. The low intensity of the XRD peaks is due to nanocrystalline nature of the film. Another reason for, no increase of intensity at 923 K may be due to re evaporation of the material from the substrate. The preferential growth of CeO_2 films along (111) and (220) crystal planes can be seen in the literature[7,8,9] . The experimental d-values of the film agreed closely with the standard values.

SEM studies

The micrographs indicate the smooth nanocrystalline nature of the films A- C as-deposited is shown in Fig. 3(a,b,c). The micrograph of the film prepared at 303 K depicts nanocrystalline nature of the film, consisting of grains in nanoscale with well defined boundaries, the grain size is found to increase with increase of substrate temperature. As the substrate temperature is increased, the surface diffusion is activated and the surface morphology improves with distinct visible grain boundaries. The particulate formation in most cases is a disadvantage and characteristic of pulsed laser deposited films and is found to be little affected in the present study also [10]. The films B and C shows nanostructured and the crystallinity of the films increase for the respective as-deposition temperatures

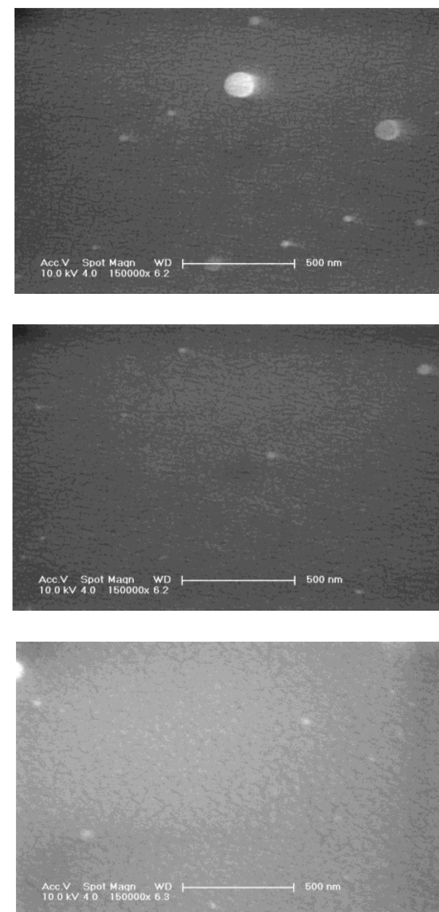

Fig. 3 SEM micrograph of CeO_2 films prepared at different substrate temperatures under an oxygen partial pressure of $2x10^{-3}$mbar.

Fig. 3 (a) and (b) shows the SEM images of A and B films with a well patterned distribution of nanocrystalline grains with porous nature. SEM images Fig. 3(c) of as-deposited C films, also show a well patterned distribution of nanocrystalline grains with grain boundary.

EDAX Studies

The elemental analysis of the film surface was made by using Energy Dispersive spectroscopy (EDS). The table shows the EDS spectrum of the film deposited at 303, 523 and 923K. No other lines besides those corresponding to Ce and O were detected. This indicates, the film don't contain any impurities. The atomic ratio of Ce/O is found to be X &Y and the weight in ratio is P & Q for films prepared at 303, 523 and 923K respectively.

Table 2 The results of EDS data of the film deposited at 303, 523 and 923 K

Sample code	Weight %		Atomic %	
	Cerium	Oxygen	Cerium	Oxygen
303K	28.16	71.84	4.28	95.72
523K	43.01	56.99	7.93	92.07
923K	47.50	52.50	9.36	90.60

Optical studies

When crystalline films are grown on amorphous substrates (like quartz) at room temperature there will be stress on the films and the films may be non-stoichiometric and hence generally show only low transmittance. The Fig. 4 shows the transmission spectrum of CeO_2 films prepared at the substrate temperatures of 303,523 and 923 K in the wavelength range of 300 to 900nm. It is observed that the transmittance of the films decreases with increase of substrate temperature. The film prepared at 303K shows the maximum transmittance of 87.817% at 550 nm. The C films show higher value of average optical transmittance compared to that of the as-deposited A and B film. This can be due to the improved crystallinity. The thickness of the films determined using interferometry technique, is found to be 72nm for the film deposited at 303K. The transmittance data obtained for the films are used to calculate the absorption coefficients at different wavelengths using the following relation

$$\alpha = \ln(1/T)t, \qquad (1)$$

where t is the film thickness and T is the transmittance of the film. The optical band gap Eg can be estimated from the following relation which is known as the Tauc plot [11]

$$\alpha h\nu = A(h\nu - Eg)^m. \qquad (2)$$

Where A is a constant, hν is the photon energy and m depends on the nature of optical transition. The value of m is (½) for direct allowed, 2 for indirect allowed The Fig. 5 (a),(b) and (c) shows the $(\alpha h\nu)^2$ vs hν plots for the CeO_2 film prepared at 303,523.923K substrate temperature respectively. The nature of the plots indicates a direct allowed transition. The bandgap of the films was determined by extrapolating the linear plot of the energy axis. The values are found to be 3.16eV, 3.25eV and 3.297eV for the films prepared at 303,523 and 923K respectively. It is found that the bandgap of the films increases with increasing substrate temperature.

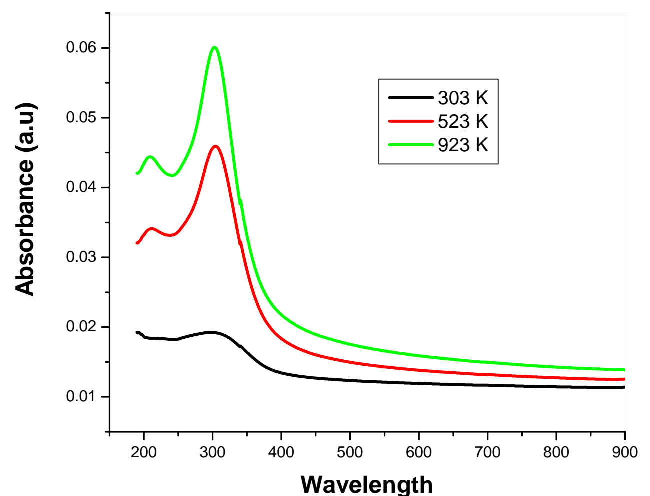

Fig. 4 The absorbance spectra of CeO_2 films prepared at the substrate temperatures of 303,523 and 923K

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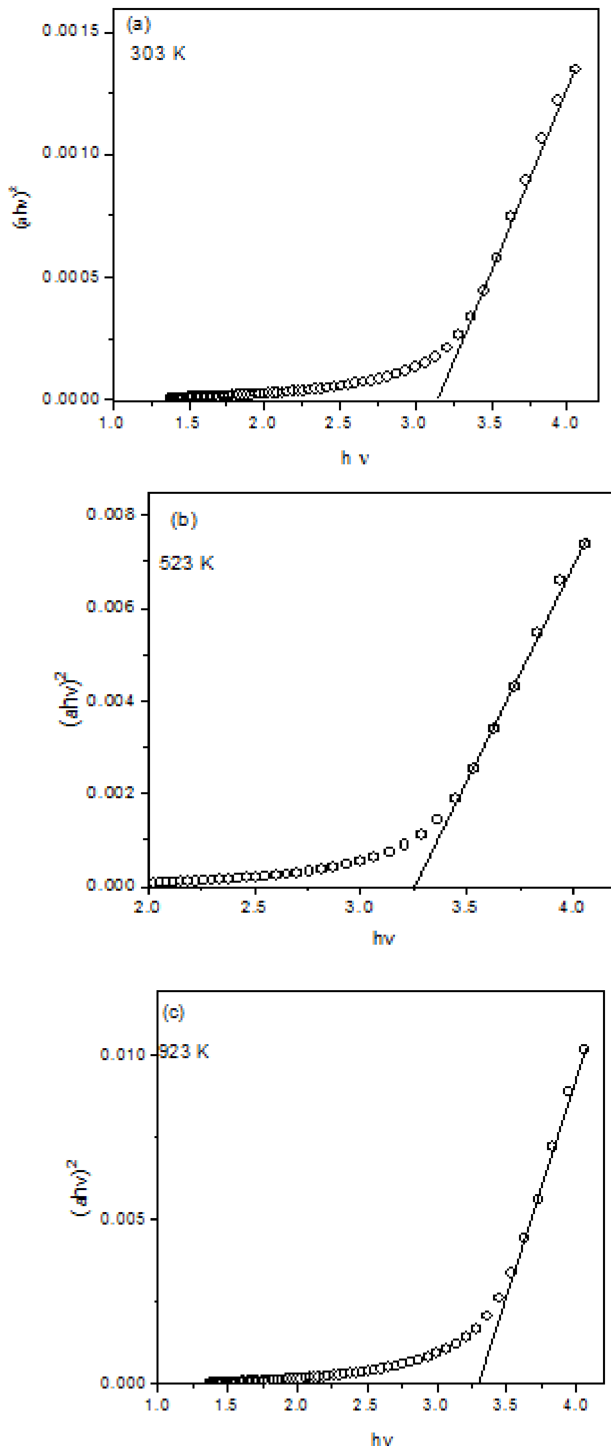

Fig. 5 the dependence of αhν vs hν of CeO_2 thin films prepared at 303, 523 and 923K.

4. Conclusion

Cerium oxide thin films were prepared using reactive pulsed laser ablation technique. The XRD studies indicate the nanocrystalline nature for the 923K substrate heated film. The XRD peaks appeared with reduced intensity and preferred orientation for (111) and (220) plane. The SEM study shows an increase in grain size and clear grain boundary with the substrate temperature. The bandgap of the films is found to increase with the substrate temperature.

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