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CHARACTERISATION OF THIN FILMS OF NOVEL IONIC CONDUCTORS PREPARED BY PULSED LASER ABLATION

Surya Narayan Padhi[1], K. Muthukkumaran[2], P. Kuppusami, E. Mohandas, V. S. Raghunathan and K. R. Hebbar[1]
Materials Characterisation Group, Indira Gandhi Centre for Atomic Research
Kalpakkam-603 102
[1]Department of Materials and Metallurgical Engineering, National Institute of Technology, Surathkal-574 157
[2]Department of Physics, Anna University, Chennai-600 025

ABSTRACT

We report the growth characteristics of cerium oxide (CeO_2) films deposited by pulsed laser ablation on <111> oriented silicon (Si) substrates over a broad range of temperature (300-1053 K), pressure ($5x10^{-5}$-0.2 mbar) and energy of the laser (200-500 mJ / pulse). The investigation showed that the films formed were polycrystalline in the entire range of substrate temperature. The grain size was found to increase with increase in the temperature up to 873 K. Above 873 K, there seemed to be an inter-diffusion occurring at the film-substrate interface. Besides, the films were found to transform from polycrystalline to amorphous structure with increase in the oxygen partial pressure from $5x10^{-5}$ to 0.2 mbar. While the films were crystalline, there were increased amount of ablated particles on the surface of the film with increase in the energy of the laser.

Key words : laser ablation, cerium oxide, thin films, x-ray diffraction.

1. INTRODUCTION

Pulsed laser deposition (PLD) is a technique that is capable of producing high quality multi - component films under a broad range of ambient conditions. There are numerous exciting applications for the high quality thin films e.g. sensors, opto-electronic devices, non-volatile random access memories etc. PLD technique has been widely used to grow thin films of numerous compounds. In particular, it enables the growth of films in reactive environments (like oxygen and nitrogen). In the preparation of materials, the optimization of the film quality in terms of deposition parameters such as substrate temperature, gas pressure, laser energy, wave length and fluence must be performed experimentally to obtain desired properties.

We demonstrate here the deposition of cerium oxide (CeO_2) on <111> oriented Si substrate using the pulsed laser ablation. Being a fluorite structure, CeO_2 has a face–centring -cubic arrangement of cations with anions occupying all the tetrahedral sites. In this structure, each cerium is surrounded by eight oxygen ions, and each oxygen ion is tetrahedrally coordinated with four cerium ions. The fluorite structure has a large number of octahedral interstitial voids. Thus, the structure is a rather 'open' one, and facilitates a rapid diffusion of oxygen ions.

Thin films of doped and undoped cerium oxide find several interesting applications, which include solid oxide fuel cells (SOFC), oxygen sensors, top coat materials for thermal barrier coatings, optical devices and buffer layer in high Tc thin films[1,2].The reason we have chosen <111> silicon as the substrate is that its lattice constant is close to the CeO_2, and the lattice

mismatch of CeO_2 with some high temperature superconductors can be as low as 1%[3,4]. These factors and its thermal and chemical properties allowed us to use CeO_2 for investigation. A great effort is being done in order to study the growth of thin films of this oxide. Although many have reported on the oriented growth of CeO_2 on different substrates by PLD, still a comprehensive understanding of the influence of the different laser and deposition parameters on the structural and physical properties of the films, has not been achieved. In particular, the final step of film formation critically depends on substrate temperature and oxygen partial pressure. In this paper, we report the formation of CeO_2 films deposited by pulsed laser ablation on <111> oriented silicon (Si) substrates over a broad range of temperature (300-1053 K), pressure ($5x10^{-5}$-0.2 mbar) and laser energy (200-500 mJ).

2. EXPERIMENTAL PROCEDURES

The deposition of CeO_2 was carried out using a KrF excimer laser with a wavelength of 248 nm (Compex 205 from Lambda Physik) and a turbo pumped deposition system. The particulars of the deposition system were: target size of 15mm diameter, target-substrate distance of 50 mm, target rotation of 6 rpm. The typical deposition conditions were: laser repetition rate of 10Hz, and energy density at the target ~2J/cm^2. Si <111> substrates of size 10mmx10mmx0.5mm were cut, cleaned in an ultrasonic cleaner and then mounted onto the heater using silver paste. In this experiment, the excimer laser is focused onto the CeO_2 target at an angle of incidence of 45°. During deposition the target was rotated and oscillated to avoid pitting. The deposition parameters used are listed in table1. The following conditions were used during deposition: (i) substrate temperatures ranging from 300 (RT) to 973K using a pulse energy of 200 mJ at a base pressure of $2x10^{-5}$ mbar (ii) partial pressure of oxygen from $5x10^{-5}$ to 0.2 mbar using a pulse energy of 200 mJ and (iii) pulse energy from 200-500 mJ/pulse at a temperature of 773K. After deposition, the chamber was cooled down to room temperature in the presence of oxygen.

The thickness of the deposited films were measured using a Dektak profilometer. The phase identification and grain size estimation were carried out using PW 1730 X-ray diffraction (XRD) system. The grain size, d_g was determined using the Scherrer formula:

$$d_g = k.\lambda / \cos\theta.\sqrt{(B^2 - b^2)} \qquad (1)$$

where λ is the wavelength (0.15418 nm), k is the correction factor (k = 0.9), θ is the diffraction angle, B is the full width at half maximum (FWHM) of the (200) diffraction line of the film, b is the FWHM of the instrumental broadening profile. A value of b = 0.175^o determined from the (200) reflection of an annealed powder sample of pure CeO_2 was used. The values of B and b were measured on the 2θ scale. Surface morphology and composition were analysed with XL30 ESEM Philips scanning electron microscope (SEM) fitted with x-ray energy dispersive analyser.

3. RESULTS AND DISCUSSION

3.1 EFFECT OF SUBSTRATE TEMPERATURE

The growth and morphology of the thin films of CeO_2 were monitored for the films grown under a vacuum of $2x10^{-5}$ mbar at an energy of 200 mJ per pulse in the temperature range 300-973 K for 1 h. The films deposited were found to be smooth and the thickness of the films was about 500 nm. Fig. 1 shows the typical XRD patterns of the films taken using CuK_α radiation. As can be seen from the figure, the film transforms from the weakly crystalline to strongly oriented films at temperatures $\geq$ 773 K. At temperatures > 873 K, peak broadening and loss of intensity are noticed due to inter-diffusion of Si with the film [5]. The lattice parameter of the films gradually decreases from 0.55 nm to 0.5414 nm in the temperature range 300-873 K, it reaches the minimum value of 0.5414 nm at 873 K and slowly starts increasing again from

0.5414 nm to 0.5490 nm in the temperature range 873-1053 K (Fig. 2). This variation in the lattice parameter might be attributed to the contribution from the growth and the thermal stresses present in the films. It was noticed that the strain is always tensile at all deposition temperature and is found to be less at 873K.The films deposited at 873 K showed a lattice parameter close to that of the bulk target (0.542 nm). Though the mismatch between the silicon substrate and the cerium oxide is small, the films are mostly polycrystalline. It is reasonable to believe that thin film of silicon dioxide on the Si substrate could have influenced the polycrystalline growth on Si substrates[6] . Fig.3 shows the variation of FWHM and grain size with substrate temperature. The grain size was found to increase from 14 nm to 62 nm because of the increase in the mobility of the adatoms with increasing substrate temperature. It is interesting to note from Fig.4 that the films are smooth, featureless, free of pores and of cracks in the entire range of deposition and the grains are found to be too small to be resolved in SEM.

3.2 EFFECT OF OXYGEN PARTIAL PRESSURE

In order to dope oxygen into cerium oxide, a series of experiments were carried out by bleeding high purity oxygen (99.99% purity) into the chamber during the ablation at a substrate temperature of 873K. Deposition at a pressure of $5x10^{-5}$, 0.05, 0.01, 0.02, 0.1 and 0.2 mbar at 873 K for a duration of 1h were carried out using a laser energy of 200 mJ per pulse. XRD analysis indicated the transformation of crystalline to amorphous film when the pressure is increased greater than 0.02mbar (Fig.5). The grain size deduced from the Scherrer relation indicated a decrease from 62 nm to 30 nm in the pressure range $5x10^{-5}$ to 0.02mbar (Fig. 6).
At increased partial pressure of oxygen (<0.02mbar), the oxygen vacancy sites are filled with oxygen and the lattice parameter and the grain size of the films reach a saturation value. Decrease in the mobility of the adatoms with increase in the oxygen seems to have reduced the crystallite size. At pressures ~ 0.2 mbar, the film transforms to amorphous structure because of the increased collision among the ablated species. This observation is in accordance with the formation of amorphous TiAlN films[7].

3.3. INFLUENCE OF LASER PULSE ENERGY

Since the rate of deposition of the CeO_2 depends on the energy of the laser beam, depositions were carried out in the energy range 200-500 mJ/ pulse at a substrate temperature of 773 K. Though the polycrystallinity is retained, the grain size has been found to be 46 nm for the energy of 200 mJ/ pulse and then it decreases to 23 nm for the energy of 400 mJ/pulse and it remains constant upto 500mJ/ pulse (Fig.7). The decrease in grain size at higher energy is attributed to the higher density of the nucleation sites with increasing deposition rate. SEM examination of the films also indicated an increased amount of particles at higher energy of the laser because of increased amount of evaporated species in the plume which subsequently coalescenced on the substrate (Fig.8).

4. CONCLUSIONS

Application of pulsed laser deposition of CeO2 on <111> oriented Si substrates has been demonstrated. The influence of the substrate temperature, oxygen partial pressure and laser energy on the growth characteristics of the oxide films was investigated. The films show mostly polycrystalline nature and they increase in size with increase in the substrate temperature. The films grown at 873 K at $5x\ 10^{-5}$ mbar was found to be crystalline; with increasing oxygen pressure, the grain size decreases and at 0.2 mbar the film was amorphous. The influence of higher laser energy at the deposition temperature of 773 K has resulted in the reduction in the grain size and formation of a few coarsened particles on otherwise smooth films.

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TABLES

TABLE 1 Typical Deposition Parameters and Conditions

Laser	KrF Excimer (248 nm)
Pulse duration	30 ns
Repetition rate	10 Hz
Pulse energy	200-500mJ/pulse
Beam size	~10mm^2
Energy density	2-5 J/cm^2
Target	Sintered CeO_2
Substrate	<111> Si
Target-substrate spacing	45 mm
Base vacuum	~2x10^{-5} mbar
Deposition time	60 min

FIGURES

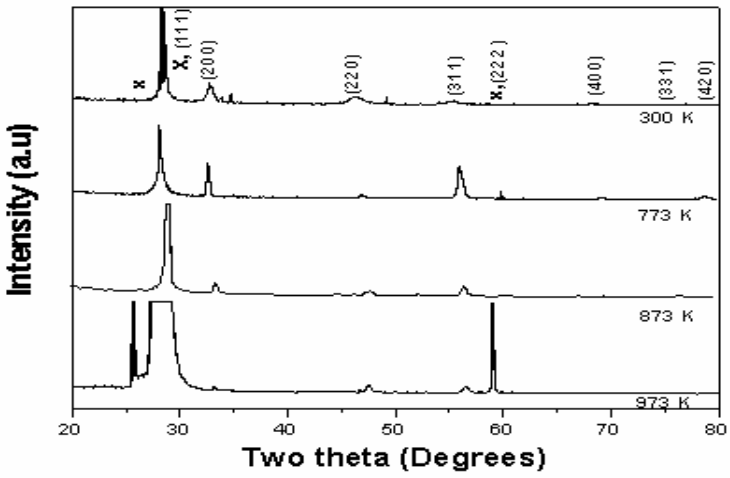

Fig. 1 XRD patterns of the films deposited at various substrate temperature using laser of 200 mJ/ pulse. x-denotes reflections from the substrate.

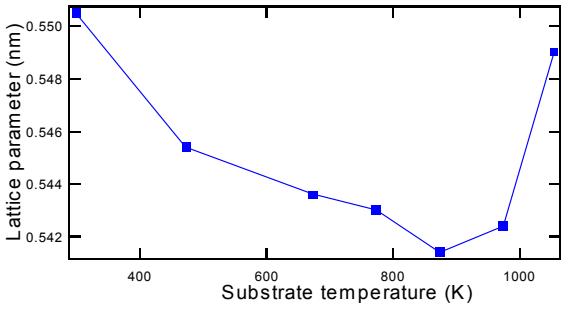

Fig. 2 Lattice parameter of the films at various substrate temperature Using a laser energy of 200mJ/pulse**.**

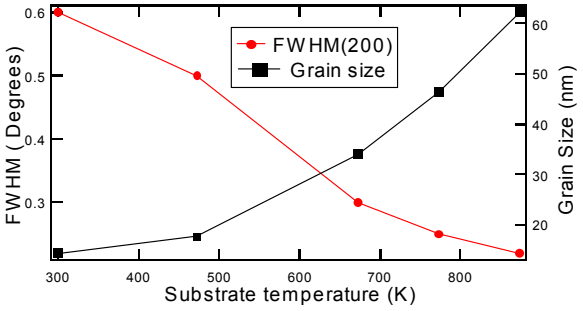

Fig. 3 FWHM and grain size of the film versus substrate temperatures.

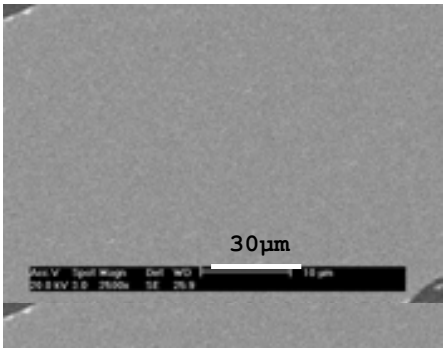

Fig. 4 SEM surface morphology of the film deposited at 873 K on Si<111>.

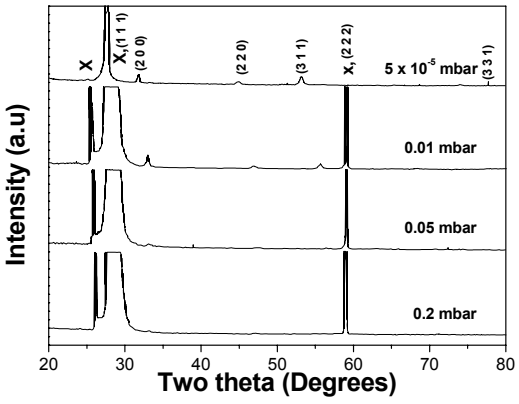

Fig. 5 XRD traces of the films deposited on <111> Si substrates at various oxygen partial pressures. x-denotes substrate peaks.

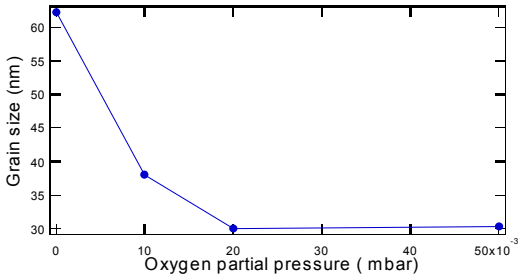

Fig. 6 Grain size versus oxygen partial pressures.

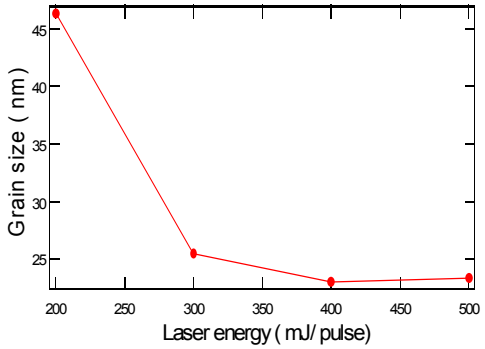

Fig.7 Grain size of CeO_2 films as function of laser energy.

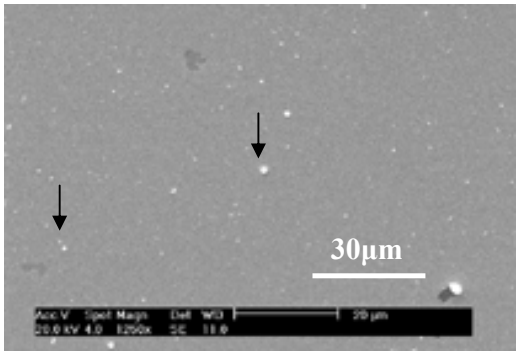

Fig. 8 SEM surface morphology of the film deposited at 773K using a laser of 500mJ/pulse.