High Temperature X-ray Diffraction (HTXRD) Studies of Ceria Thin Films Prepared by Pulsed Laser Deposition

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Abstract

The ceria thin film was deposited on Si (100) at an optimized oxygen partial pressure of 3.0 x 10^{-2} mbar at room temperature. The thickness of the film was measured and it was found to be ~1µm. To examine the phase stability and thermal expansion behaviour of CeO_2 thin film, the high temperature x-ray diffraction (HTXRD) was employed in the temperature range RT-1273 K. The HTXRD pattern revealed that in all the temperatures (RT-1273 K), the film showed polycrystalline nature and having cubic phase. The HTXRD pattern showed excellent thermal stability in the temperature range of study. The lattice parameter and unit cell volume have been calculated as a function of temperature. The mean linear thermal expansion coefficient was calculated as a function of temperature and it was found to be 10.16x10^{-6} K^{-1} in the temperature range RT-1273 K.

Key words: Thin films, Cerium oxide, Pulsed laser deposition, High temperature x- ray diffraction, Mean linear thermal expansion coefficient.

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1. Introduction

Cerium oxide has high refractive index, high melting point, large dielectric constant, wide band gap, high transparency in the VIS-NIR regions, chemical stability and thermal stability [1,2]. Thorium is expected to play an important role in the third stage of the Indian nuclear reactor program [3]. A research on lattice thermal expansion behaviour of different thoria based systems is relevance to thorium oxide based nuclear reactors. Thermal expansion is an important parameter in the performance of a nuclear fuel-pin assembly. The main difficulties while investigating the PuO_2 based systems are its high radioactivity and toxicity which require extensive safety precautions. One way to overcome this problem is to use CeO_2 in place of PuO_2 as they have similar physico–chemical properties (ionic radii, melting points, enthalpy of formation, specific heat and thermal expansion coefficient etc.) Thus the plutonium chemistry can be well simulated using CeO_2 in place of highly active PuO_2 [4,5]. It is also a promising material for fast oxygen sensors at high temperature because of its chemical stability and high diffusion coefficient of oxygen vacancies. The coatings of rare earth oxides like, La_2O_3, CeO_2, Pr_2O_3 and Nb_2O_5 have lower thermal diffusivity, phase stability, high melting point,chemical inertness and high thermal expansion coefficient and hence they have potential as TBC materials [6].

In this work, thin films of CeO_2 were deposited on Si (100) substrates at room temperature and at an oxygen partial pressure of $3x10^{-2}$ mbar by pulsed laser deposition (PLD) using ceria target. PLD is a simple and unique technique [7] to prepare high quality thin films from a wide variety of materials and compounds. One of the main advantages of PLD is the generation of hyper thermal species with high kinetic energy of the order of 100 eV. Deposition of hyper thermal species can enhance the adatom

mobility and hence the film quality. High temperature x-ray diffraction (HTXRD) was employed to study the structural changes in the CeO_2 film as a function of temperature HTXRD provides the information about variation of lattice parameters and hence average linear thermal expansion coefficients of the ceria thin films.

2. Experimental Procedures

Commercially available CeO_2 (99.99% purity) powder was compacted into a pellet of 25 mm diameter and 4 mm thickness at a pressure of 10 MPa using a uni-axial press. These pellets were sintered at 1673 K for 5 hours. The sintered pellet was used as a target for PLD. Prior to the deposition of CeO_2 thin films, the chamber was evacuated to $2x10^{-5}$ mbar using a turbo molecular pump backed with a rotary pump. The target was rotated and translated with an electric motor to avoid pitting on the target. The CeO_2 thin film was deposited on Si (100) substrates at an optimized oxygen partial pressure of $3x10^{-2}$ mbar at room temperature using the KrF excimer laser (λ=248 nm), energy density of $3J/cm^2$ and a repetition rate of 10 Hz. The thickness of the films was measured by the Dektak profilometer (DEKTAK 6M-stylus profiler by Veeco, USA). The structural changes of the deposited films were studied using INEL XRG – 3000 x-ray diffractometer (XRD) fitted with M/s Buehler high temperature (HT) camera HDK 2.4 and a curved position sensitive detector. The ceria thin film deposited on Si (100) substrate (of size 10mm x10mm) was placed over a tantalum strip, which served as a sample stage as well as heating element. A W-Re thermocouple was used for measuring the temperature of the sample. The XRD patterns were recorded in the temperature range RT -1273 K at the interval of 100 K in vacuum of the order of ~ $2x10^{-5}$ mbar. The heating rate of 10 K/min, cooling rate 25 K/min and soaking time of 5 minutes were followed. XRD patterns were recorded at set temperature for 30 minutes in parallel

recording mode. The unit-cell parameters were determined using a least-squares refinement program. The average linear thermal expansion coefficients were calculated in the temperature range 300 –1273 K.

3. Results and Discussion

The thickness of the films deposited was measured and it was found to be ~ 1 μm. The sintered ceria pellet was used as the target for thin film deposition. The XRD pattern of the pellet showed the phase pure CeO_2 having cubic structure (a= 0.541 nm) (JCPDS No. 34-0394) [2]. HTXRD was employed on the ceria films in the temperature range of RT-1273 K to study the thermal stability and thermal expansion. Fig.1 shows the HTXRD patterns of the CeO_2 film and showed the peaks at an angle (2θ) of 28.55°, 33°, 47.4°, 56.3°, 59°, 69.4°, and 76.7° and these peaks are corresponding to the phase pure CeO_2 having cubic structure (JCPDS No. 34-0394). The peak intensity of (111), (200), (220) and (311) reflections were higher and the FWHM of these reflections decreased with the increase of temperatures.

The crystallite size was found to increase from 10 to 44 nm along (111) reflection, as the substrate temperature was raised from RT to 1273 K, and it increased from 21 to 98 nm along (200) orientation. The crystallite size has increased from 11 to 58 nm along (220) direction and it was 13-57 nm range along (311) reflection. Thus, it is seen that the crystalline growth was maximum along (200) orientation.

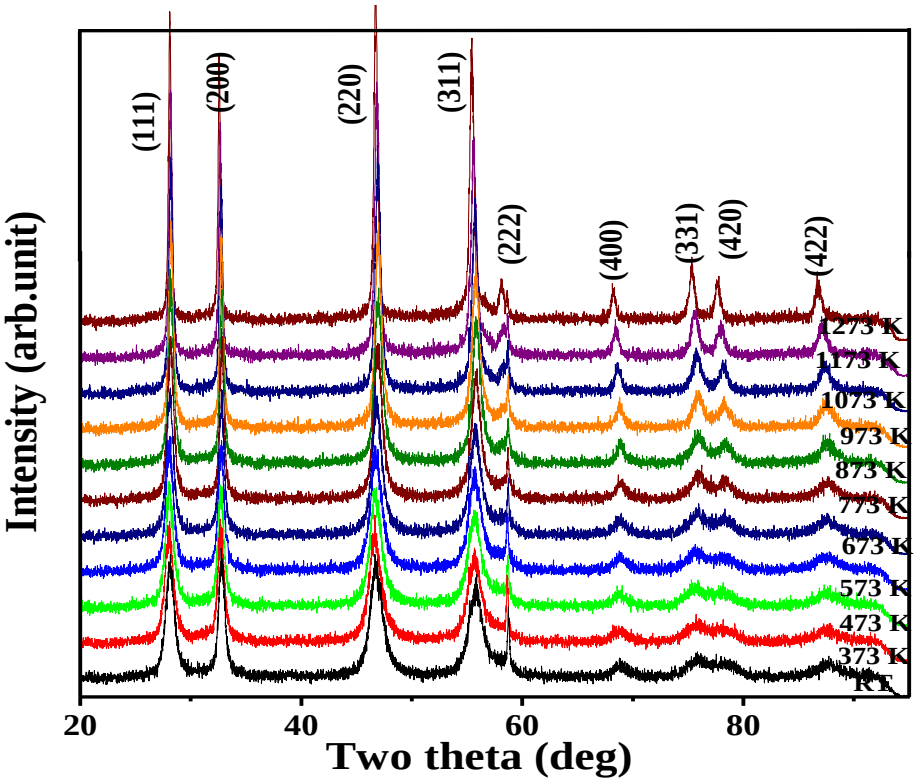

Fig.1. HTXRD profiles of the ceria thin film scanned in vacuum in the temperature range RT - 1273 K.

Lattice parameters were calculated as a function of temperature. The experimentally obtained lattice parameter data were fitted to third degree polynomial with temperature increment (T-300). The corrected lattice parameters were used for calculating thermal expansion coefficients.

$a=5.446+7.07143\times10^{-5}(T-300)-8.38071\times10^{-8}\ (T-300)^2+4.49827\times10^{-11}(T-300)^3$

The corrected lattice parameters for various temperatures are given in Table.1. The unit cell volume was also calculated using the corrected lattice parameters.

In cubic structure, the lattice parameter, *a*, was found to vary from 5.446 Å to 5.480 Å as the temperature was increased from RT to 1273 K. Once the lattice parameters are known as a function of temperature, it is possible to estimate the percent thermal expansion and mean linear thermal expansion coefficients.

The variation of percent linear thermal expansion along $a = \left(\frac{\Delta a}{a}\right) x100$ and percent volume (lattice) thermal expansion (v) with temperatures was calculated. The maximum linear thermal expansion of 0.6 % was observed at 1273 K and the maximum percent lattice thermal expansion (volume) was 2% at the same temperature. There was no phase change in the temperature range 300-1273K. Hence the film showed excellent thermal stability throughout the temperature range of study. The mean thermal expansion coefficient of the cubic phase ceria has been calculated using the following expression [8]:

$$\alpha_a = \frac{1}{a_{RT}}\left[\frac{a_T - a_{RT}}{T - RT}\right]$$

The mean linear thermal expansion coefficient and volume thermal expansion coefficients were calculated and are presented in Table.1. The mean linear thermal expansion is found to be 10.16×10^{-6} K^{-1} (298-1273 K). The mean volume thermal expansion coefficient is 30.51×10^{-6} K^{-1}.

Table 1. Temperature versus lattice parameters and thermal expansion coefficients

Temperature (K)	a (corrected) (Å)	V ($Å^3$)	α_a x10^{-6} (K^{-1})	α_v x 10^{-6} (K^{-1})
298	5.446	161.522	------	------
373	5.4543	162.262	20.95	62.759
473	5.4595	162.726	14.39	43.087
573	5.4635	163.084	11.82	35.423
673	5.4666	163.362	10.16	30.540
773	5.4690	163.577	8.95	26.897
873	5.4710	163.757	8.03	24.148
973	5.4729	163.927	7.35	22.124
1073	5.4749	164.107	6.88	20.703
1173	5.4773	164.323	6.60	19.864
1273	5.4804	164.602	6.51	19.597

It was reported that the thermal expansion coefficient of the pure ceria was found to be 10.9 x10^{-6} K^{-1} in the temperature range 298-800 K [9]. Mathew et al [10] investigated the bulk and lattice thermal expansion studies on $Th_{1-x}Ce_xO_2$ (x=0.0, 0.04, 0.08 and 1.0) using dilatometry and HTXRD. The average linear thermal expansion coefficient of CeO_2 was found to 11.58x10^{-6} K^{-1} and 11.76 x10^{-6} K^{-1} using dilatometry and HTXRD studies respectively [10]. The values obtained in the present study are in agreement with the other reported values [9,10]. Due to its excellent thermal stability and higher thermal expansion coefficient, the ceria films can be used for high temperature applications.

4. Conclusions

In the present study phase stability, crystallite size, lattice parameter changes and thermal expansion coefficient of ceria thin films deposited on (100) Si has been investigated using HTXRD in the temperature range RT-1273 K. The HTXRD revealed that the film contained ceria of cubic phase and showed excellent thermal stability in the entire range RT-1273 K. The crystallite sizes of the ceria along different reflections were calculated and the film preferred more along (200). The average linear thermal expansion coefficient and mean lattice thermal expansion coefficient was found to be 10.16x10^{-6} K^{-1} and 30.51x10^{-6} K^{-1} respectively.

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