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Role of C ion implantation on structural and optical properties of CeO₂ thin films deposited on quartz substrates

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Abstract

This investigation reports on effect of C ion implantation on structure and optical properties of CeO₂ thin films deposited on quartz substrates by the radio frequency (RF)-sputtering method. X-ray diffraction analysis shows that the face-centered cubic (FCC) structure corresponds to CeO₂. The lattice parameter of C ion implanted CeO₂ films was found to decrease compared to that of the pristine CeO₂ film. The shift in the peak positions after C ion implantation indicates changed lattice parameters. The observed values of strain are found to be positive and decreasing value of strain after C ion implantation indicates tensile strain in all of the prepared CeO₂ films. The Raman spectra further confirm the formation of phase and also indicate the presence of defects in these films. The F_{2g} peak intensity is decreasing with C ion fluence compared with that of the pristine film which is due to defects created after C ion implantation. Uv-Vis spectra shows that energy band gap decreases with C ion implantation which indicates increase in conductivity with C ion implantation in the films.

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1. Introduction

Ceria based metal oxide materials have several technological applications and has been extensively studied [1-5]. These materials are important because of their potential applications such as UV absorbents and filters, electronic ceramic, ultra-precise polishing, gas sensor, catalysts and electrolyte in the fuel cell technology [6], catalytic wet oxidation, engine exhaust catalysts and photocatalytic oxidation of water. Most recently, CeO₂ nanoparticles have been tested for their ability to serve as free-radical scavengers [7-8]. Therefore, the extensive synthesis and study of CeO₂ becomes an urgent task for further research and applications [9-10]. Cerium oxide (CeO₂) shows good optical properties and is a semiconductor with wide band gap energy (3.19eV).

The material's modification with energetic ion beams shows interesting technological applications. There are two modes of materials modification by energetic ion beams, ion

implantation and swift heavy ion (SHI) irradiation. In both of the techniques, the energy and fluence of incident ions play an important role [11]. In the ion implantation process, the energetic ions have low energy (a few tens of keV to a few hundreds of keV). The desired ions can be implanted in the suitable material by choosing the various implantation parameters like type of ion, ion energy, range of ion and ion fluence etc. and the materials properties get modified due to the presence of implanted ions. There are several reports available on the formation of embedded nano phases of target ions and effects of such nano phases on the various properties of host material [12-13]. In this context we have performed ion implantation experiment with different fluencies on CeO₂ thin films.

Considering the importance of these materials, present study focuses on understanding of structural and optical properties of C ion implanted CeO₂ thin films deposited by RF sputtering.

2. Experimental details

The CeO₂ thin films were deposited on quartz substrates using the radio frequency (RF)-sputtering technique. The sputtering was performed in an argon (Ar) gas environment at room temperature with 150W sputtering power. The deposited films were then implanted with 70 keV C ions using the Low Energy Ion Beam Facility (LEIBF) at the Inter University Accelerator Center (IUAC), New Delhi, with fluencies of 1×10^{16} ions cm⁻² and 3×10^{16} ions cm⁻². The structural and optical properties of the C implanted films were investigated. The crystalline structure of these films was studied by x-ray diffraction (XRD) measurement using a Bruker D8 x-ray diffractometer (CuK α radiation; $\lambda=1.54$ Å). To further confirm the phase and defects such as oxygen vacancies, Raman measurement was carried out using a Renishaw inVia Raman microscope ($\lambda=514$ nm). Further, the optical properties were examined using a UV-Vis (Hitachi U-3300) spectrometer at room temperature.

3. Results and Discussions

3.1 XRD Analysis:

Fig.1. shows the XRD patterns of pristine and C ion implanted CeO₂ thin films. The XRD patterns of all the films show the fluorite-like FCC structure of CeO₂. It is observed that the intensity of significant (111) planes increases after C ion implantation, which indicates the increased crystallinity of the films compared with pristine film. The most prominent (111) planes are used to obtain the average crystallite size using Scherrer's equation [14],

$$D=0.9\lambda/\beta\cos\theta$$

Where D is the crystallite size, λ (1.54 Å) is the wavelength of the incident x-rays, β is the full width at half maximum (FWHM) and θ is the Bragg angle of reflection. The crystallite size values are shown in table 1. The observed lattice constant of the pristine CeO₂ film (5.478 Å) is larger than that for bulk CeO₂ (5.411 Å) (JCPDS-75-0390). Further, the lattice parameter of C ion implanted CeO₂ films was found to decrease compared to that of the pristine CeO₂ film. The shift in the peak positions after C ion implantation indicates changed lattice parameters, and these are clearly visible in the XRD pattern. The difference between the ionic radii of C (0.260 nm) and O (0.140 nm) contributed to the decrease in the lattice parameters due to lattice contraction after C ion implantation [15]. These changes in the lattice parameters led to lattice strain, implying the modification of various physical properties. The strain ' ϵ ' is estimated using the following relation [16],

$$\epsilon=\beta\cos\theta/4$$

The observed values of strain are found to be positive and to decrease after C ion implantation, as shown in table 1. The positive value of strain ϵ indicates tensile strain in all of the prepared CeO₂ films. The difference between the substrate's thermal coefficient and that of the deposited material might be the reason for this.

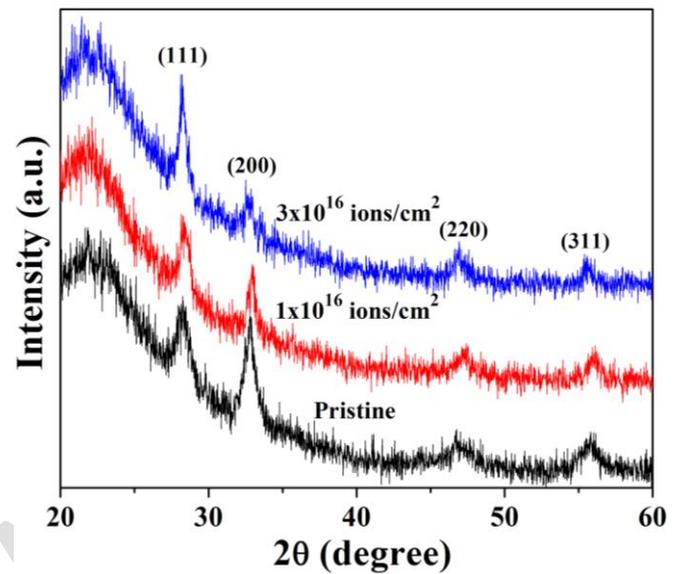


Fig. 1. XRD pattern of pristine and C ion implanted CeO₂ thin films.

3.2 Raman measurement

To examine the effect of C ion implantation on the local structure, defects and stress/strain in materials Raman spectroscopy was carried out at room temperature and is shown in fig. 2.

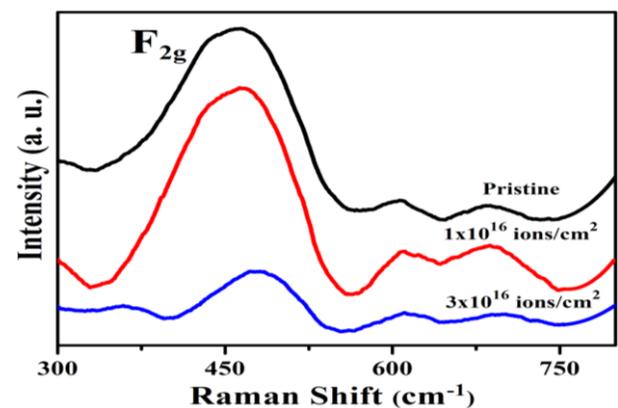


Fig. 2. Raman spectra of pristine and C ion implanted CeO₂ thin films.

Table 1. Various calculated parameters of pristine and N ion implanted CeO₂ thin films.

Composition	Lattice Parameter, 'a' (nm)	Crystallite size (nm)	Strain (ϵ) $\times 10^{-4} \text{ lin}^{-2} \text{ m}^{-4}$	Band gap Energy (eV)
Pristine	5.478	10.22	36.929	3.4
1x10 ¹⁶ ions/cm ²	5.447	13.15	28.699	3.18
3x10 ¹⁶ ions/cm ²	5.470	14.20	26.573	3.04

Fig. 2 shows the formation of a typical FCC structure for CeO₂. The peak observed at 443–463 cm⁻¹ is attributed to the Raman-active vibrational mode (F_{2g}) of CeO₂, and corresponds to the symmetrical breathing mode of oxygen ions around each Ce⁴⁺ cation (O–Ce–O) [17]. A small shift in the F_{2g} peak towards higher wavelength and broadening in the FWHM is observed as a result of C ion implantation. These structural changes in the Raman spectra are attributed to inhomogeneous strain and defects [18]. It is evident from fig. 2 that the F_{2g} peak intensity is decreasing with C ion fluence compared with that of the pristine film.

3.2 Optical Properties

The UV–Vis spectra of pristine as well as C ion implanted CeO₂ thin films are shown in Fig. 3. Band gap energy is presented in Table 1.

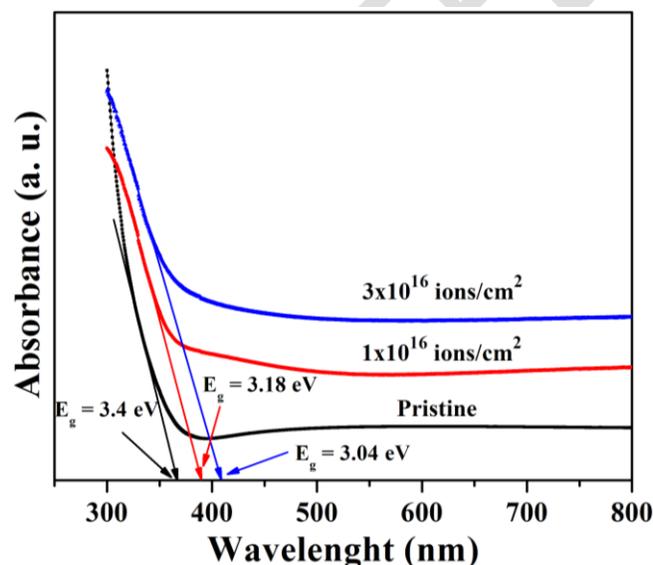


Fig.3. UV-visible spectra of pristine and C ion implanted CeO₂ thin films.

From table 1 it is evident that energy band gap decreases with C ion implantation. In other words, there is increase in conductivity with C ion implantation fluence. Due to C ion implantation, band gap decreases due to increase in the density of states which indicates that the correlation length in the conducting network is increasing. This observation indicates that due to C ion implantation in CeO₂, the electronic property in the system is driven by the induced disorder effect.

4. Conclusions

In this work, we investigated the effect of C ion implantation on structural and optical properties of CeO₂ thin films deposited on quartz substrates by the radio frequency (RF)-sputtering method. The CeO₂ thin films were implanted with C ion at fluences of 1x10¹⁶ and 3x10¹⁶ ions cm⁻². These films were characterized using XRD, Raman spectroscopy and UV-Vis spectroscopy. The XRD and Raman results confirmed the formation of FCC structure in all these CeO₂ films. The presence of defects in pristine and C ion implanted films were observed clearly in the Raman results. Energy band gap was found to be decreasing with C ion implantation.

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