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Swift heavy ion irradiation induced nanoparticle formation in CeO_2 thin films

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ABSTRACT

Nanoparticle formation in the, rf-sputtering grown, polycrystalline CeO_2 thin films is achieved by the swift heavy ion (SHI) irradiation. Crystal structure and phases present in the as-grown and irradiated thin films are investigated by the X-ray diffraction (XRD) measurements. Irradiation induced formation of spherically shaped nanostructures, on the film surface, is confirmed by the atomic force microscopy (AFM). The Raman spectra of the irradiated samples show increased line-width and peak position shifting in the Raman active mode (F_{2g}) of CeO_2, indicative of the nanocrystallization in the irradiated CeO_2 thin films. Formation of nanostructures in the irradiated samples is also briefly discussed in the light of ion energy and energy loss mechanisms.

1. Introduction

Nano-science/technology has become an attractive area of research as the nanodimensional systems/materials possess outstanding properties (i.e., optical, mechanical and electronic, etc.) and hence functionalities. The physicist finds nanomaterials as the quantum mechanically confined system where as the confinement in the dimensions is predictable by the size of the nanoparticle. The quality of altering all the physical and chemical properties by the small variation in size of the nanodimensional systems make them extremely suitable for a large variety of applications. There are various synthesis methods (i.e., sol–gel, co-precipitation, sputtering, laser ablation, and ion implantation/irradiation, etc.) by which doped and un-doped nanostructures can be synthesized [1–5]. In the field of nano-science/nanotechnology, the energetic ions are of use for, both, synthesis and modification [4,5] of the nanomaterials. The important issues in the nanomaterial synthesis are the (i) tailoring of shape of nanostructures, (ii) control of the size of particles and (iii) the size distribution. Ion beams play a significant role related to all these issues [5,6]. There are two ways of nanostructuring by ion beams namely; ion implantation and ion irradiation. In the ion implantation process the energetic ions have low energy (few tens of keV to few hundred keV). The desired ions can be implant in the suitable matrix by choosing the various implantation parameters like; type of ion, ion energy, range of ion, and ion fluence, etc. The synthesis of nanoparticles by ion implantation poses few problems. First, when ions are implanted at low energies, their depth is very less and intersects the surface so that incoming ions may sputter previously implanted ions. When the ion fluence is increased (in low energy regime), the concentration of implanted element saturates. On the other hand, if the energy of the implanted ions is higher (to overcome problem of sputtering of implanted atoms), the duration of the implantation may be prohibitive because the concentration at the mean range decreases in inverse proportion to the profile width, which varies almost in proportion to the ion energy. Another major problem with ion implantation is the non-uniform size distribution of the so formed nanoparticles. This arises due to the concentration depth gradient of implanted atoms. Some efforts have been made to achieve a narrower size distribution of nanoparticles in the insulating and semiconductor materials via implantation followed by post annealing [4,6]. In contrast to nanostructuring by ion implantation the SHI irradiation induced nanocrystallization has emerged as more reliable and interesting technique. In case of SHI irradiation, the incident ions have velocity comparable to the orbital velocity of electrons of the target atoms. The energetic ions lose their energy by two distinct energy deposition processes; (i) electronic energy loss and (ii) nuclear energy loss. The electronic energy loss (S_e or $(dE/dx)e$) is due to the inelastic collisions of the impinging ions with the atoms of the target material and this process dominant in the high energy regime (energy >1 MeV/nucleon) of the incident ion. On the other hand, the nuclear energy loss (S_n or $(dE/dx)n$) is due to the elastic collisions of the incident ions with the target atoms and dominant in the low energy regime (energy of few keV/nucleon) of the incident ions. If material's thickness is very less than the range of the projectile ions, the overall energy loss or the

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energy deposited by SHI beams is ascribed to the electronic energy loss process rather than the nuclear energy loss process. As a consequence of high energy deposition, within a very short span of time, track of molten zone is formed along the ions trajectory. This molten zone solidifies within the picoseconds. As a result of the rapid quenching of the material, nanocrystallization may take place within the matrix [6] or even near the surface of the sample [7].

Among the various known transparent conducting oxide materials (e.g., ZnO, SnO_2, and In_2O_3, etc.) cerium oxide (CeO_2) is one of the important candidate which have unique cubic crystal structure and high k-dielectric constant. CeO_2 having a optical band gap of 3.3 eV and *n*-type carrier density which make it a promising candidate for various technological applications such as a buffer layer in silicon on insulator devices [8], basis in the field effect transistors [9], high k-dielectric in the capacitors [10,11], catalysis [12], coating material [13], and electrolysis [14], etc. Attempts have, therefore, been made to improve its properties, and hence functionalities, by (i) creating nanostructures [15–17], (ii) transition metal ion doping [18–20] and (iii) bombarding with swift heavy ion (SHI) beams [21,22]. In case of ion irradiation effects on CeO_2, this material is adopted for the simulation of radiation damage in oxide fuels (like; UO_2, having same fluoride type crystal structure as of CeO_2) in nuclear reactors which are subjected to high-energy particles interaction [23,24]. Although, some preliminary studies on the ion beam induced structural changes in crystalline films [25] and powder pellets [26] have been reported, but a detailed study on the SHI irradiation induced nano-crystallization and densification in the CeO_2 thin films has not been carried out so far. In the present study, we report the synthesis of CeO_2 thin films, on Si substrate, using RF-sputtering technique and their subsequent irradiation with 175 MeV Au ion beams at different irradiation fluences. We observed that irradiation at low irradiation fluence start to form narrow size distribution of particles. At the higher irradiation fluence spherical shaped and closely packed nanoparticles have been observed on the film surface. The formation of smaller sized nanocrystallites, in the irradiated thin films, is briefly discussed on the basis of energy loss mechanism, and experimental findings of XRD, AFM and Raman scattering measurements.

2. Experimental

CeO_2 ceramic targets, used in this work, were prepared from the commercial CeO_2 powders (Sigma–Aldrich, 99.9% purity). The circular target of the diameter of ~50 mm was formatted in a mould using a uni-axial pressure of 300 MPa. The target was sintered at 900 °C, in air, using a thermal cycle corresponding to a temperature upward and downward slope of 150 °C/h with a plateau of 2 h at maximum temperature (900 °C). The substrates (quartz) were cleaned with trichloro-ethylene and then acetone and methanol using an ultrasonic cleaner. The well cleaned substrates were loaded in the growth chamber having the base pressure of $\sim 6 \times 10^{-4}$ Pa. The oxygen and argon gases were used (O_2:Ar = 1:2) as the oxidizing reactant and the plasma generation gas, respectively. The sputtering power was 200 W and the substrates were kept at 600 °C temperature, during the deposition. The growth time was kept constant for all the samples. After the deposition the films were cooled down slowly to room temperature under the oxygen partial pressure of 240 Pa. After deposition, the film thickness was measured by a profilometer and found to 200 ± 10 nm. The well characterized CeO_2 thin films were irradiated with 175 MeV Au^{13+} ions beams with two different fluences of 1×10^{12} ions/cm^2 and 5×10^{12} ions/cm^2 at room temperature using 15UD Tandem Accelerator at Inter-University Accelerator Center (IUAC) New Delhi, India. The ion beam was focused to a spot of 1 mm × 1 mm and scanned over an area of 10 mm × 10 mm using a magnetic scanner to achieve fluence uniformity across the sample area which was typically 5 mm × 5 mm. The fluence values were measured by collecting the charge falling on the sample mounted on an electrically insulated sample holder placed in secondary electron suppressed geometry. Ladder current was integrated with a digital current integrator and the charged pulses were counted using scalar counter. The structural study on un-irradiated and irradiated samples was done by glancing angle XRD using Brooker D8 advanced diffractometer with Cu Kα radiation (λ = 1.540 Å). Surface morphology was studied by AFM using digital Nanoscope IIIa SPM, in tapping mode. The Raman scattering measurements were performed using In-Via Raman microscope. Excitation was provided by an argon-ion laser of wavelength 514 nm and a low incident power to avoid thermal effects.

3. Results and discussion

Fig. 1(a)–(c) shows the glancing angle XRD pattern (plotted in log scale) of as deposited and irradiated thin films. The irradiation fluence, used to irradiate the sample, is mentioned in each panel of the figure. It is visible from the Fig. 1 that a high intense peak at $2\theta = 28.055^{\circ}$ with two low intense peaks at $2\theta = 47.2^{\circ}$ and $2\theta = 59.02^{\circ}$ are observed in as-deposited and irradiated thin films. These peaks are assigned to (1 1 1), (2 2 0) and (2 2 2) plane of CeO_2, having fluorite type structure (JCPDF#750390). It is visible from Fig. 1 that the intensity of the XRD peaks (e.g., peak (1 1 1)) is continuously decreased with increase of ion irradiation fluence. Beside this, the full width at half maximum (FHWM) of the XRD peaks is improved with increase in the irradiation fluence (see Fig. 1(d)). The average grain size is calculated by using the Scherrer relation; $D = 0.9\lambda/\beta\cos\theta$, where D is the average grain size, λ is the wavelength of the used X-rays, and β is the FWHM of the diffraction peak. Thus calculated particle size is 13.82 nm, 11.86 nm and 9.72 nm for the as-deposited, 1×10^{12} ion/cm^2, and 5×10^{12} ion/cm^2 irradiated CeO_2 thin films, respectively. It is clear that the crystalline size continuously decreased with increase in the irradiation fluence. The observed changes in the particle size, FWHM, and the XRD peak position may help us to understand the impact of SHI irradiation on the other structural properties like; lattice parameters values and strain present in the thin films etc. We calculated the lattice parameter (a) of as-deposited and irradiated thin films using the relation; $a = d_{(hkl)}\sqrt{(h^2 + k^2 + l^2)}$, where d is the inter-planner distance and (hkl) is the miller index. The calculated unit cell parameters are found to 5.507 Å, 5.438 Å and 5.419 Å, respectively. This helps us to conclude that the cell parameter, and hence, unit cell volume shrink with increase the irradiation fluence. The percentage strain is calculated using the relation $\sigma = \left(\frac{a_{substrate} - a_{film}}{a_{substrate}}\right) \times 100$ [27]. Where, $a_{substrate}$, and a_{film} are the lattice parameters of substrate and film, respectively. The positive value of σ corresponds to the tensile strain (the cell is elongated in the films plane and compressed along the out of plane growth direction). Whereas the negative value of σ corresponds to the compressive stress (the cell is compressed in the films plane and elongated along the out of plane growth direction). Thus calculated strain comes to −1.77, −0.498 and −0.147, for the as-deposited 1×10^{12} ion/cm^2, and 5×10^{12} ion/cm^2 irradiated CeO_2 thin films, respectively. It is clear from the calculations that the compressive strain is abridged with increasing the irradiation fluence. The net deduction in the lattice strain may cause the densification in the film material. Thus, our XRD results help us to conclude that ion irradiation, with different fluence, lead to (i) shrink in the unit cell parameter/volume, (ii) net deduction in the strain and, interestingly, (iii) generate smaller sized particles.

To further examine the SHI irradiation induced formation of smaller sized particles in CeO_2 thin films, systematic, AFM measurements were performed on the as-deposited and irradiated thin