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Studies of the electronic excitation modifications induced by SHI of Au ions in RF sputtered ZrO_2 thin films

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ABSTRACT

In the present study, Zirconium oxide thin films of 150 nm were grown by RF magnetron sputtering at room temperature. The prepared thin films annealed at 550 °C and irradiated with SHI of 120 MeV Au^{9+} ions by varying ion fluence between 1×10^{11} to 1×10^{13} ions/cm^2. The modifications induced by SHI irradiation in structural, surface morphological, optical and chemical properties of the thin films have been characterized by X-ray diffraction (XRD), Atomic Force Microscope (AFM), UV–Visible spectroscopy, Fourier transform infrared spectroscopy (FTIR), Photoluminescence (PL) and Rutherford backscattering (RBS). XRD result shows the formation of monoclinic and tetragonal phase with the change in the intensity of the peak is observed due to SHI irradiation. AFM measurements ensure that the grain size lies in the range of 33–46 nm and root mean square roughness increases up to a fluence of 5×10^{11} ions/cm^2 then decrease for the higher fluence. Photoluminescence (PL) emission peaks were obtained at 456, 488 and 516 nm when the pristine and irradiated ZrO_2 thin films are excited with 300 nm light. The obtained peak in Rutherford Backscattering Spectrometry (RBS) confirms the presence of Zr and O atoms in the samples.

1. Introduction

Zirconia (ZrO_2) has been a fascinating material for more than two decades with its unique properties such as high refractive index, low optical loss, wide band gap, high transparency, high tensile strength and low brittleness etc. [1–5]. Because of its significant properties, it is considered as best candidate for various application such as high reflectivity mirrors, wear resistant protective coatings, laser mirrors, broadband interference filters, optical and oxygen sensors [6–8]. It is considered as high dielectric material with high permittivity ε_r (~ 22) possess good thermal stability with Si. Hence it is considered as most compatible and promising material for fabrication of very-large-scale-integrated (VLSI) circuits [9,10] as well as ZrO_2 thin films are well studied in field effect transistors (FET) and dynamic random access memories (DRAMs), and etc. [11,12]. The high performance thin gate dielectric layers of high integrated circuit density is required by the microelectronic industries. Since SiO_2 as gate oxide dielectric has limitations due to large energy consumption and rapidly rise in tunneling currents. Among many candidates ZrO2 is preferential substitute to maintain the tunneling current and to reduce the large energy consumption [13–15]. ZrO_2 displays its existence in three different phases: (i) monoclinic; (ii) tetragonal; (iii) cubic. Moreover, monoclinic phase is stable at room temperature and it undergoes tetragonal phase transformation at higher temperature (above 1170 °C). Tetragonal ZrO_2 transforms to another structural phase, i.e., cubic phase (~ 2370 °C) [16,17].

In addition, zirconium oxide thin films prepared by different techniques including Physical vapor deposition [18], electron beam deposition [19], atomic layer deposition [20], chemical bath deposition [21], chemical vapor deposition [22], anodization [23], DC [24] and RF [25] sputtering may results in different physical, chemical and electronic properties. Fig. 1 describe the clear objective of present work. The zirconium oxide thin films have been prepared by RF sputtering technique. These films have been irradiated by 120 MeV Au^{9+} highly energetic ion beam to investigate the modifications induced in structural, surface morphological and optical properties of the samples. The irradiation of the ZrO_2 was carried out with different ion fluence ranging from 1×10^{11} to 1×10^{13} ions/cm^2. Therefore, the various characterizations such as X-ray diffraction (XRD), Atomic force microscopy (AFM), UV-Visible, Fourier-transform infrared spectroscopy (FTIR), photoluminescence (PL) and Rutherford backscattering spectrometry (RBS) have been done in the present study. Radiation response of highly energetic ions on the solid materials helps to understand the modification induced in the properties of the materials in constructed

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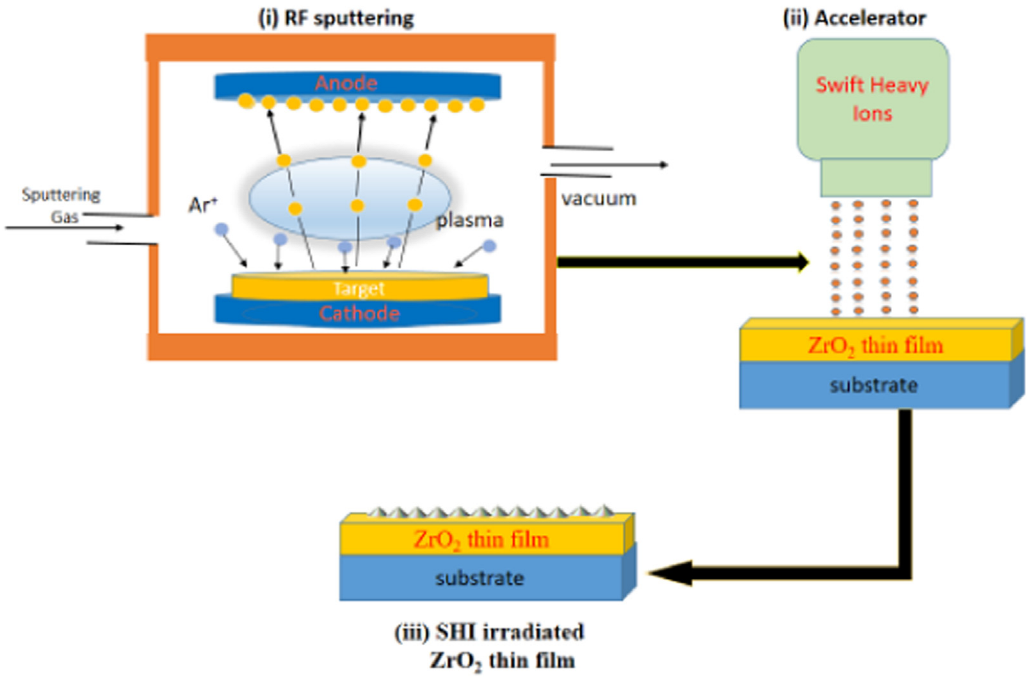

Fig. 1. Schematic diagram illustrates the experimental work (i) synthesis of ZrO_2 thin films by RF sputtering technique (ii) swift heavy ion irradiation using accelerator and (iii) modification induced in irradiated zirconium oxide thin films.

ways [26]. An energetic incident ion traversing in material loses its energy mainly by elastic and inelastic collision called nuclear and electronic energy loss (dominant at high energy) respectively [27,28]. Two models, i.e., (1) Coulomb explosion and (2) thermal spike are accounted for description of the electronic energy loss (S_e) caused by swift heavy ions [29–31]. The radiation effect of insulating material such as zirconium oxide, ranging from few KeV to MeV results in modification in structural, optical, morphological, thermal and electrical properties [32–35]. A lot of of work has been reported to understand the influence of irradiation in zirconium oxide. Benyagoub reported that the swift heavy ion (250 MeV I) beam induced phase transformation from monoclinic to tetragonal in zirconium oxide. As a consequences, it was found that the electronic energy loss with the transition temperature at thermal equilibrium is responsible for the phase transformation which is consistent with thermal spike model [29]. Kurpaska et al. studied the effect of 150 KeV Ar^+ ion implantation on the functional properties of zirconium oxide. They concluded that the ion fluence affect the position of Raman bands and nanohardness of monoclinic and tetragonal phase increases with increasing ion fluence [36]. Manzini et al. investigated the effect of 70 MeV I ion beam radiation on mesoporous and nanocrystalline mixed phase of ZrO_2 thin films. They reported that SHI irradiation weakly changes the phase composition and no change in crystallographic parameters were observed [37]. Several reports of different materials such as BaF_2 [38], Fe_3O_4 [39], $Mo_{0.98}Fe_{0.02}O_3$ [40], TiO2 [41] and SnO_2 [42] are available for the modifications in various properties of the nanoparticles thin films by swift heavy ion irradiation [43]. Moreover, Sorieul et al. have observed the increase in optical absorbance and Urbach energy attributed to the damage accumulation due to 4 MeV Xe-ion irradiation in Silicon carbide samples [44]. Bolse et al. investigated the 350–600 MeV Au ion induced dewetting in NiO, Fe_2O_3 thin films. They studied that the dewetting patterns in the metal oxides resemble with the molten polymer deposited on Si which was assured by the SEM and AFM study [45]. Kluth et al. reported the formation of fine structure in ion tracks in thermally grown SiO_2 layers by highly energetic ion irradiation of ^{197}Au ions using the energy between 27.4 and 185 MeV [46]. The choice of ZrO_2 thin films is such as that it has high dielectric constant and low leakage current level and radiation induced zirconium oxide can be used for various electronic applications [47,48].

2. Experimental procedure

2.1. Sample preparation and irradiation

The samples were prepared using RF sputtering system with 99.95% purity zirconium target. These ZrO_2 thin films were deposited on Si wafer and glass substrate. The deposition was done at room temperature. The gaseous plasma of Ar gas (with high purity 99.97%) was formed and the sputtering pressure was kept at 5×10^{-1} Pa. The thin films were prepared using the sputtering power of 600 W and the vacuum chamber was evacuated to the base pressure of 5×10^{-5} mbar with a turbo molecular pump. The substrate and target distance was maintained at 60 mm. Before deposition, the substrates were carefully cleaned for 30 min by double distilled water, ethanol and acetone using sonication process and dried by flowing nitrogen (N_2) gas. The thickness of the thin films were determined by surface profilometer and the prepared samples were annealed at 550 °C for 12 h. and named as pristine. The annealed ZrO_2 thin films with dimension 1 cm × 1 cm were irradiated by 120 MeV Au^{9+} ions at different fluences 1×10^{11}, 5×10^{11},1×10^{12}, 5×10^{12} and 1×10^{13} ions/cm^2 using 15 UD Pelletron accelerator at Inter University Accelerator Centre (IUAC), New Delhi, India. The irradiation was carried out at room temperature under high vacuum (~ 10^{-6} mbar) with maintaining the beam current of 1 pnA to avoid the effect of target heating during SHI irradiation. The ion beam was scanned in X-Y plane using electromagnetic scanner on the surface of the samples to obtain dose uniformity across the thin films. The projected range of 120 MeV ions irradiated samples was calculated using the SRIM simulation program 2008 [49]. The calculated projected range is much higher than the film thickness (150 nm) which reveals that whole passage of ions is overwhelmed by electronic energy loss(S_e). Thus, the bombarding ions come to the rest in substrate after passing through the surface of the sample. During SRIM simulation, the density of the films was taken 5.6800E+ 00 g/cm^3 = 8.3284E + 22 atoms/cm^3. The longitudinal and lateral straggling of these samples is 5746 Å and 7199 Å respectively. The values of electronic (S_e) and nuclear (S_n) energy losses for ZrO_2 are $S_e = 2.624 \times 10^3$ (eV/Å)