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Full Length Article

Effect of 500 keV Ar^{2+} ion irradiation on structural and magnetic properties of TiO_2 thin films annealed at 900 °C

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ABSTRACT

Present study investigates the structural and magnetic properties of TiO_2 thin films prepared by electron beam evaporation technique, annealed at 900 °C and irradiated with 500 keV Ar^{2+} ions. The films before irradiation exhibit anatase phase. Irradiation leads to diffused XRD peaks indicating amorphisation of the anatase phase at the fluence of 1×10^{14} ions/cm^2. Increasing the fluence to 5×10^{16} ions/cm^2 leads to evolution of brookite phase out of the amorphous TiO_2. In addition, an impurity phase, Ti_4O_7 is observed in pristine as well as in irradiated films, which show radiation resistant behavior to 500 keV Ar^{2+} ion irradiation upto the highest fluence 5×10^{16} ions/cm^2. Anatase to brookite phase transformation followed by an intermediate amorphous phase occurs without showing either grain growth or change in film thickness as evidenced from Atomic Force Microscopy (AFM) and Rutherford's Back Scattering (RBS) measurements, respectively. Further, both pristine and irradiated films exhibit ferromagnetic behavior at room temperature (RT) irrespective of their phase and crystallinity. The difference in magnetization observed in pristine and film irradiated at ion fluence 5×10^{16} ions/cm^2 is ascribed to the difference in oxygen vacancies.

1. Introduction

Titanium dioxide (TiO_2) thin films have been found to be a charming oxide in current years, due to environmental friendly nature, high refractive index, simple fabrication and high chemical stability, application in semiconductor devices, high dielectric constant and low cost [1–8]. Therefore, it is very important to study the evolution of different physical, chemical and magnetic properties of TiO_2, particularly in thin films prepared by different techniques, and also by post deposition treatments. Variation of the properties of thin films primarily depends on various deposition techniques such as chemical vapor deposition, solvothermal process, reactive sputtering, pulsed laser deposition, electron beam evaporation etc [9–18]. Electron beam evaporation technique is a unique physical vapor deposition technique, where, one can obtain high purity sample with high rate of deposition. Besides the synthesis techniques, one may also modify the structure as well as the properties of the films by means of energetic ion beams with energy ranging from few keV to GeV [19]. Energetic ions, while traversing through a material medium, loose energy through two processes. These are electronic energy loss, S_e and nuclear energy loss, S_n. In the former process, the energy is lost by inelastic collisions of the incident ions with the electrons of the target material. In the later process, the energy is lost by the elastic collisions of the incident ions with the nuclei of atoms in the material. The parameters of the ion beam which play a vital role in defect engineering and modification of materials are the energy deposited per unit length and the ion fluence. The domination of either of the two energy losses (S_e and S_n) in modifying the properties of the material depends on the mass and energy of the incident ions. For example, in MeV range of ions energy, S_e induced processes dominate, which can coherently excite electrons in highly localized region around the ion path and amorphise if the S_e exceeds (S_{eth}) a material dependent threshold value. In keV range, S_n induced processes dominate and leads to creation of atomic size point defects and cluster of defects in the target [20–25]. In many situations ions can go beyond their disordering role and induce transformations from one crystalline structure to another [26–35]. Structural transformation is reported by Thakur et al. [36] in TiO_2 thin films after irradiating with 200 MeV Ag ions. Ishikawa et al. [37], irradiate TiO_2 thin films with 230 MeV Xe^{15+} ions and 200 MeV Au^{13+} ions and have observed decrease in intensity of (0 0 4) peak corresponding to anatase phase. After irradiating with 200 MeV Ag^{15+} ions, Thakur et al. [38] have observed transformation of paramagnetism to ferromagnetism in TiO_2 thin films. Irradiating with 100 MeV Ag^{7+} ions, we have studied the structural and magnetic properties of cobalt doped TiO_2 thin films where films show

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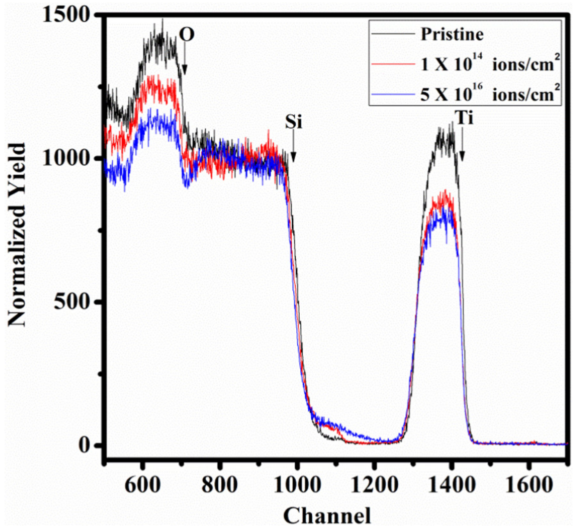

Fig. 1. Oxygen resonance RBS spectrum taken with α particles, of thin films annealed in O_2 environment at 900 °C and irradiated with 500 keV Ar^{2+} ions.

amorphous nature at highest fluence (1×10^{12} ions/cm^2) and ferromagnetism at RT in films irrespective of phase and crystallinity [39]. Khanam et al. [40] have explained that ripple patterns are observed on TiO_2 film after irradiating with 80 keV Xe^+ ion due to formation of vander-waal crystals. Majumder et al. [41] show fabrication of nanodots by irradiating rutile TiO_2 film with Ar ions. Transformation of self-assembled crystalline TiO_2 nanorod to amorphous layer on irradiating with 50 keV Ar^+ ions is shown by Saini et al. [42]. It has been shown by Ramana et al. [43] that 1.5 keV Ar^+ ions induce amorphisation of the $KTiOAsO_4$ surface by partial loss of As from the surface of the material as well as reducing As^{5+} to As^0. Similarly, Atuchin et al. [44] have also found in $KY(WO_4)_2$ that Ar^+ ion irradiation results amorphisation and reduction of W^{6+} to W^0 with partial loss of K. Phase transformation from anatase to brookite phase and higher magnetization in higher roughness film due to higher oxygen vacancies has also been reported by Bharati et al. [45]. Although there are bunch of reported literatures on irradiation effect in TiO_2, rare studies on structural and physical properties under low energy ion irradiation are reported.

Here, we have irradiated TiO_2 thin films deposited through e-beam evaporation technique and annealed in oxygen environment at 900 °C with 500 keV Ar^{2+} ions. The structure dependent magnetic properties in pristine and irradiated films have been examined with varying ion fluence from 1×10^{14} to 5×10^{16} ions/cm^2. In addition to Ti_4O_7, we have shown an unusual anatase to brookite phase transformation with increasing ion fluence. Pristine as well as irradiated films show ferromagnetic behavior at room temperature irrespective of their phase and crystallinity. The difference in magnetization observed in the pristine film (A) and in the irradiated film (C) is attributes to the difference in oxygen vacancy.

2. Experimental details

At room temperature TiO_2 thin films were deposited by electron beam evaporation technique on Si (n-type (1 0 0)) substrate. Before deposition, the substrates were consecutively washed in acetone, trichloroethylene (TCE), alcohol and finally by distilled water. Base vacuum of the chamber prior to the deposition was maintained at $\sim 1.1 \times 10^{-6}$ mbar. Deposition pressure (P_d) was fixed at $\sim 4 \times 10^{-5}$ mbar. Rate of deposition was kept at 0.2 nm/s. 20 mA current was supplied to the electron gun throughout deposition. High purity TiO_2 (99. 99%, STREM Chemicals, USA) target was used for the deposition of the film. With the help of flowing water, copper crucible was cooled which contain TiO_2 ingot. The distance between the substrate and target was kept at 14 cm. After deposition, the films were annealed under high purity O_2 gas at 900 °C in a tubular furnace for 1 h and were cooled to room temperature.

Thin films of dimension 1 × 1 cm^2 were irradiated in the Material Science Beam line under high vacuum using 500 keV Ar^{2+} ion with a steady beam current of 7500 nA accessible from the 10 GHz Electron Cyclotron Resonance (ECR) ion source, at IUAC, New Delhi, India. Beam current per unit charge is called as particle nanoampere (pnA). Therefore, the beam current for Ar^{2+} ion in terms of pnA was calculated to be 3750 pnA. Films were irradiated with the ion fluence (ions per unit area) 1×10^{14} and 5×10^{16} ions/cm^2. Beam was scanned in the x-y plane to expose the entire film. Henceforth, the pristine film, films irradiated at an ion fluence of 1×10^{14} and 5×10^{16} ions/cm^2 referred as film A, B and C respectively were characterized by using X-ray diffraction (XRD), Raman Spectroscopy, Rutherford Backscattering Spectroscopy (RBS) and Atomic Force Microscopy (AFM).

The structure of the film was determined by X-ray diffraction (Brucker D8 Advance) using CuKα radiation (λ = 1.5406 Å, current = 40 mA, voltage = 40 kV) at a glancing angle of α = 0.5°. The phase of the film was further determined from Micro-Raman Spectroscopy. The surface morphology was studied with Atomic Force

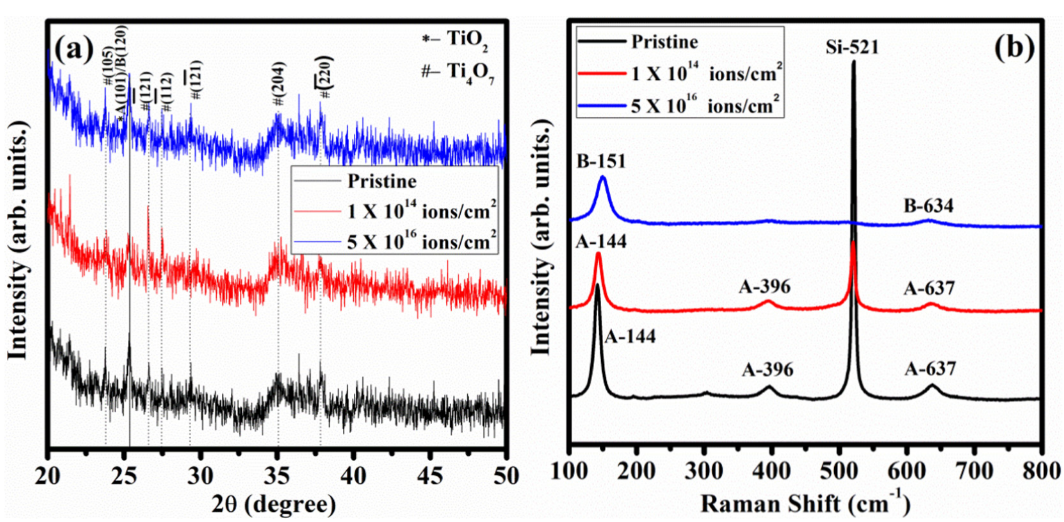

Fig. 2. (a) GAXRD pattern of TiO_2 thin films annealed in O_2 environment at 900 °C and irradiated with 500 keV Ar^{2+} ions, (b) Raman spectra of films before and after ion irradiation.