Applied Surface Science 428 (2018) 723–729

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

500 keV Ar^{2+} ion irradiation induced anatase to brookite phase transformation and ferromagnetism at room temperature in TiO_2 thin films

B. Bharati [a], N.C. Mishra [b], D. Kanjilal [c], Chandana Rath [a,*]

[a] School of Materials Science and Technology, Indian Institute of Technology (BHU), Varanasi, 221005, India
[b] Department of Physics, Utkal University, Bhubaneswar 751004, India
[c] Inter University Accelerator Center, Aruna Asaf Ali Marg, New Delhi 110067, India

ARTICLE INFO

Article history:
Received 2 June 2017
Received in revised form 6 August 2017
Accepted 9 September 2017
Available online 22 September 2017

Keywords:
TiO_2 thin films
Low energy ion irradiation
e-beam evaporation technique

ABSTRACT

In our earlier report, where we have demonstrated ferromagnetic behavior at room temperature (RT) in TiO_2 thin films deposited through electron beam evaporation technique followed by annealing either in Ar or O_2 atmosphere [Mohanty et al., Journal of Magnetism and Magnetic Materials 355 (2014) 240–245], here we have studied the evolution of structure and magnetic properties after irradiating the TiO_2 thin films with 500 keV Ar^{2+} ions. The pristine film while exhibits anatase phase, the films become amorphous after irradiating at fluence in the range 1×10^{14} to 1×10^{16} ions/cm^2. Increasing the fluence up to 5×10^{16} ions/cm^2, amorphous to crystalline phase transformation occurs and the structure becomes brookite. Although anatase to rutile phase transformation is usually reported in literatures, anatase to brookite phase transformation is an unusual feature which we have reported here for the first time. Such anatase to brookite phase transformation is accompanied with grain growth without showing any change in film thickness evidenced from Rutherford's Back Scattering (RBS) measurement. From scanning probe micrographs (SPM), roughness is found to be more in amorphous films than in the crystalline ones. Anatase to brookite phase transformation could be realized by considering the importance of intermediate amorphous phase. Because due to amorphous phase, heat deposited by energetic ions are localized as dissipation of heat is less and as a result, the localized region crystallizes in brookite phase followed by grain growth as observed in highest fluence. Further, we have demonstrated ferromagnetic behavior at RT in irradiated films similar to pristine one, irrespective of their phase and crystallinity. Origin for room temperature ferromagnetism (RTFM) is attributed to the presence of oxygen vacancies which is confirmed by carrying out XPS measurement.

1. Introduction

Titanium dioxide (TiO_2) thin films have been found to be a fascinating oxide in recent years, due to environmentally benign, because of its high refractive index, chemical stability, relatively high energy conversion efficiency, dielectric constant, excellent transparency in visible and near IR region [1–8]. The variety of properties basically depends on various deposition techniques such as reactive sputtering, chemical vapor deposition, solvothermal process, pulsed laser deposition, electron beam deposition technique etc [9–20]. One of the unique physical vapor deposition techniques is e-beam deposition where high purity sample is deposited with high rate. Besides the synthesis techniques, one may also modify the structure as well as properties by using energetic ion beams with energy ranging from keV to GeV [21]. Interaction of energetic ions and material looses energy by two processes such as electronic energy loss, Se and nuclear energy loss, Sn. In the former process, the energy is lost by inelastic collisions of the electrons of the target material with the incident ions. In the later process, the energy is lost by the elastic collisions of atoms in the material with the incident ions. The parameters, of the ion beam, which play central role in defect engineering, are the energy deposited per unit length and the ion fluence. Depending on the energy and mass of the ions, either Se or Sn dominates in modifying the properties of the material. For example, in keV range, Sn induced processes dominate and leads to creation of atomic size point defects and cluster of defects in the target [22–26]. Therefore, post deposition effects of energetic ions on structural properties of different materials have been of cur-

* Corresponding author.
E-mail address: chandanarath@yahoo.com (C. Rath).

http://dx.doi.org/10.1016/j.apsusc.2017.09.070
0169-4332/

rent interest [27–34]. Ishikawa et al. have irradiated TiO_2 films with 230 MeV Xe^{15+} and 200 MeV Au^{13+} ions having fluence of 2.5×10^{12} and 2×10^{12} ions/cm^2 and have observed decrease in intensity of (004) peak of anatase phase [35]. Thakur et al. report structural transformation in TiO_2 thin films irradiated with 200 MeV Ag ions [36]. Trasformation of self-assembled crystalline TiO_2 nanorod to amorphous layer is shown by Saini et al. on irradiating with 50 keV Ar^+ ions [37]. Thakur et al. report transformation of paramagnetism to ferromagnetism in TiO_2 thin films after irradiating with 200 MeV Ag^{15+} ions [38]. In our earlier report, we have studied the structural and magnetic properties of cobalt doped TiO_2 thin films before and after irradiating with 100 MeV Ag^{7+} ions [39]. In spite of the reported literatures on irradiation effect in TiO_2, meager literatures are found on low energy ion irradiation induced structural and physical properties of TiO_2.

Here, we examine the effect of 500 keV Ar ion irradiation on TiO_2 deposited through e-beam evaporation technique and have examined the structure dependent magnetic properties of pristine and irradiated films. We have shown an unusual transformation from anatase to brookite phase through an intermediate amorphous phase. Pristine as well as irradiated films show ferromagnetic behavior at RT irrespective of their phase and crystallinity.

2. Experimental details

TiO_2 thin films have been deposited at room temperature using electron beam evaporation technique on Si (*n*-type (100)) substrates. Before deposition, the substrates were subsequently, boiled in acetone, trichloroethylene (TCE), alcohol and distilled water for cleaning and then finally dried. Prior to the deposition the base vacuum of the chamber was maintained at $\sim 1.1 \times 10^{-6}$ mbar. $\sim 4 \times 10^{-5}$ mbar pressure fixed as the deposition pressure (P_d). The deposition rate was kept at 0.2 nm/s. During deposition, 20 mA current was supplied to the electron gun. High purity TiO_2 (99.99%, STREM Chemicals, USA) target was used for the evaporation purpose. Copper crucible was cooled by constant circulation of water in which TiO_2 ingot was placed. The distance between substrate and target was kept 14 cm. After deposition, the films were annealed under constant flow of high purity O_2 gas at 500 °C in a tubular furnace for 1 h and then the furnace was cooled to room temperature. The films were cut into 1×1 cm^2 and used for ion irradiation study. The thin films were irradiated in the Material Science beam line under high vacuum using 500 keV Ar^{2+} ion with a stable beam current of 7500 nA available from the 10 GHz Electron Cyclotron Resonance (ECR) ion source, at IUAC, New Delhi, India. Particle nanoampere (pnA) is defined as the total beam current per unit charge. So the beam current in terms of pnA for Ar^{2+} ion was calculated to be 3750 pnA. The fluence (ions per unit area) was varied in the range from 1×10^{14} to 5×10^{16} ions/cm^2. The films will be referred as A (Pristine), B (1×10^{14} ions/cm^2), C (1×10^{15} ions/cm^2), D (5×10^{15} ions/cm^2), E (1×10^{16} ions/cm^2) and F (5×10^{16} ions/cm^2), respectively. Hereafter, X-ray diffraction (XRD) and Raman of all the films were carried out and confirmed the phase of the films.

The structure of all the films 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 films was also confirmed from Micro-Raman Spectroscopy. The thickness were measured using Rutherford's backscattering spectroscopy (RBS) using α particles (He^{2+}) of energy 2 MeV. The surface morphology was studied with Scanning Probe Microscope (SPM) from Nova Instruments. Imaging was done in SPM mode with the help of noncontact non conducting (NCNC) tip. Software employed for analyzing SPM image was Novapx supplied by Nova Instruments. Further, magnetic properties of the films were investigated using a SQUID VSM (from Quantum Design). X-ray photo-emission spectroscopy (XPS) measurements of the films were carried out using MgKα radiation. Thin films were handled with Teflon forceps and utmost care has been taken during measurements to avoid the possible magnetic contamination in the films.

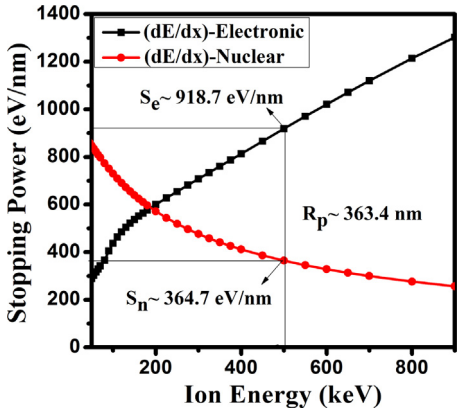

Fig. 1. Electronic and nuclear energy loss as a function of energy for argon ion on the TiO_2 target.

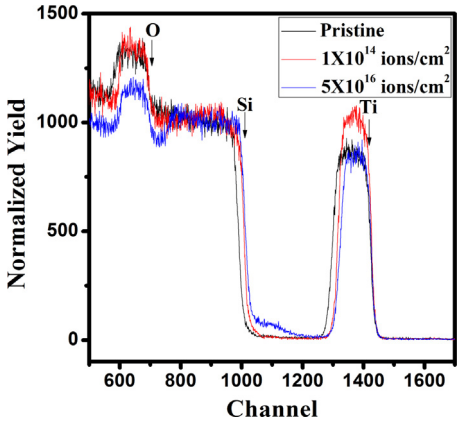

Fig. 2. RBS spectra of TiO_2 thin films A, B and F indicating Ti, Si and O edges.

3. Results and discussion

Irradiating TiO_2 thin films with 500 keV Ar^{2+} ions, we have studied structural evolution and post irradiation defects induced damage. The electronic energy loss (Se), nuclear energy loss (Sn) and projected range (Rp) calculated using SRIM code shown in Fig. 1 are found to be 918.7 eV nm^{-1}, 364.7 eV nm^{-1} and 363.4 nm respectively. Fig. 2 depicts the RBS spectra of pristine film (A), film irradiated with $1 \times {}^{14}10$ ions/cm^2 (B) and with 5×10^{16} ions/cm^2 (F). Besides Ti, Si and O, no other elements have been detected from the RBS spectra in either pristine or irradiated films. Thickness of the film obtained from the width of Ti curve is around 360 nm which does not change after irradiation. As the film thickness matches with the projectile range, one may expect the defects created in surface of the film as well as in Si substrate. Fig. 3 depicts the glancing angle X-ray diffraction (GAXRD) patterns of the films A to F. Pristine film, A, is crystalline in nature showing diffraction peaks at 25.33°, 37.91° corresponding to (101), (004) of anatase phase of TiO_2 (JCPDS PDF# 894921). After irradiating with the ion fluence of 1×10^{14} ions/cm^2 (B), 1×10^{15} ions/cm^2 (C), 5×10^{15} ions/cm^2 (D) and 1×10^{16} ions/cm^2 (E), film shows amorphous nature. Film after irradiating with ion fluence 5×10^{16} ions/cm^2 (F) exhibits crystalline nature. The diffraction peaks in