Available online at www.sciencedirect.com
SCIENCE DIRECT®
Nuclear Instruments and Methods in Physics Research B 250 (2006) 250–253
NIM B
Beam Interactions with Materials & Atoms
www.elsevier.com/locate/nimb

Structural changes in anatase TiO_2 thin films irradiated with high-energy heavy ions

N. Ishikawa [a,*], S. Yamamoto [b], Y. Chimi [c]

[a] Research Group for Irradiation Field Materials, Japan Atomic Energy Agency (JAEA), Tokai-mura, Ibaraki 319-1195, Japan
[b] Research Group for Inorganic Functional Materials, Japan Atomic Energy Agency (JAEA), Takasaki-shi, Gunma 370-1292, Japan
[c] Research Group for Irradiation Field Materials, Japan Atomic Energy Agency (JAEA), Tokai-mura, Ibaraki 319-1195, Japan

Available online 21 June 2006

Abstract

In order to investigate possible structural changes due to high-density electronic excitation, anatase TiO_2 thin film specimens were irradiated with 230 MeV $^{136}Xe^{15+}$ ions and 200 MeV $^{197}Au^{13+}$ ions. X-ray diffraction (XRD) patterns were measured before and after irradiation. The intensity of the XRD peak assigned to the (004) planes of anatase TiO_2 decreases in an exponential manner as a function of ion-fluence. This result can be explained by the formation of the cylindrical damaged regions (i.e. ion tracks) with diameters of 9.6 and 16.3 nm for 230 MeV Xe and for 200 MeV Au ion irradiations, respectively. The difference in the track diameter between Xe ion irradiation and Au ion irradiation can be attributed to the difference in the electronic stopping power (and to the ion-velocity effect, if any). For 200 MeV Au ion irradiation, splitting of the (004) peak is observed. The original (004) TiO_2 peak remains in the same position, but the new peak shifts to higher angles as fluence increases.

PACS: 61.10.Nz; 61.72.Dd; 61.80.Jh; 61.82.Ms

Keywords: Irradiation effect; X-ray diffraction; Ion track; Electronic excitation effect; TiO_2

1. Introduction

Structural changes due to high-density electronic excitation have been extensively studied for various oxides irradiated with high-energy heavy ions. The characteristic feature of the structural change is the formation of continuous tracks along ion paths. The size of the track is one of the parameters used to quantify the damage due to the high-density electronic excitation. It can be estimated by means of direct observation methods such as transmission electron microscopy (TEM) [1,2] and atomic force microscopy (AFM) [3,4], while indirect measurement methods are also available such as Rutherford backscattering spectroscopy in channeling geometry (RBS/C) [5,6], Mössbauer spectroscopy [7], small-angle X-ray scattering (SAXS) [8,9] and wide-angle X-ray diffraction (XRD) [10–14]. The XRD method has been applied for the estimation of track size in polymers [10,11] and some oxides [12–14]. In this study, the XRD method is applied to estimate the track size for titanium dioxide, TiO_2.

TiO_2 exists in three different crystalline phases: anatase, rutile (both tetragonal) and brookite (orthorhombic). To date, only rutile and anatase have been observed in thin TiO_2 films. When the substrate temperature during deposition is below 150 °C, amorphous TiO_2 films are often observed [15,16]. Since the rutile phase is the most thermodynamically stable among the three phases, many experimental and theoretical investigation have been carried out on rutile phase including the effect of high-energy ion irradiation [17]. In contrast to extensive studies on the rutile phase, very little is known about the anatase phase. Another feature of the anatase phase is that it transforms to rutile phase by thermal treatment above 700–900 °C [18], indicating its thermally unstable nature. Since

* Corresponding author. Tel.: +81 29 282 5472; fax: +81 29 282 6716.
E-mail address: ishikawa.norito@jaea.go.jp (N. Ishikawa).

0168-583X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.nimb.2006.04.119

high-density electronic excitation is known to be a trigger for the formation of metastable crystallographic phases [13,14,19], the possibility for irradiation-induced phase transformation of TiO_2 should also be examined. Thus, in this study we investigate the effects of irradiation of anatase TiO_2 with high-energy heavy ions.

2. Experimental procedure

The samples used in the present experiment were TiO_2 thin films with the anatase structure. The specimens were epitaxially grown single crystal thin films of TiO_2 with $\langle 001\rangle$ $TiO_2 \parallel \langle 001\rangle$ $SrTiO_3$ prepared by a pulsed laser deposition method. The thickness of the films was 0.3 μm. Irradiation with 230-MeV $^{136}Xe^{15+}$ ions and 200-MeV $^{197}Au^{13+}$ ions was performed at room temperature in the tandem accelerator at Japan Atomic Energy Agency, Tokai Research and Development Center (JAEA-Tokai). The maximum fluence for 230-MeV Xe ions and 200-MeV Au ions was 2.5×10^{12} ions/cm^2 and 2.0×10^{12} ions/cm^2, respectively. Irradiation was performed along the direction perpendicular to the film surface that is parallel to the *c*-axis of TiO_2.

Before irradiation, the diffraction peak assigned to the (004) plane of anatase TiO_2 was observed as shown in Fig. 1. The *c*-axis lattice parameter estimated from the position of (004) peak of unirradiated anatase TiO_2 films is $c = 9.5$–9.6 Å. The electronic stopping power and the projected range were estimated using SRIM-2003 [20,21]. Since the projected range for 230-MeV Xe ions (15 μm) and 200-MeV Au ions (13 μm) is larger than the film thickness (0.3 μm), defects are uniformly introduced along the sample thickness and the possibility of ion implantation can be excluded.

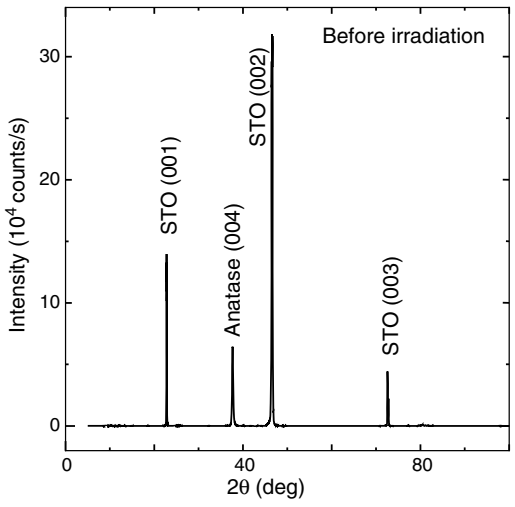

Fig. 1. Typical X-ray diffraction pattern of unirradiated anatase TiO_2 film deposited on $SrTiO_3$ (STO) substrate.

3. Results and discussion

Fig. 2 shows the evolution of the (004) anatase TiO_2 reflection, before and after irradiation with 230-MeV Xe ions (Fig. 2(a)) and 200-MeV Au ions (Fig. 2(b)). A monotonic decrease in XRD peak intensity is observed with increasing ion-fluence for both irradiations. In order to demonstrate whether there is any irradiation-induced change in peak position or in the full width at half maximum (FWHM) of the peak, the XRD intensities shown in Fig. 2 were normalized by the maximum intensity value of the peak. The results are shown in Fig. 3. As can be clearly seen in Fig. 3(a), for the 230-MeV Xe ion irradiation, almost no shift of XRD peaks is observed up to the fluence of 2.5×10^{12} ions/cm^2. This indicates that there is no detectable change in the average *c*-axis lattice parameter within the experimental error, which we estimated $\leqslant 0.1\%$ of the *c*-axis lattice parameter. Also, almost no change in the FWHM of the (004) reflections was observed to a fluence of 2.5×10^{12} ions/cm^2.

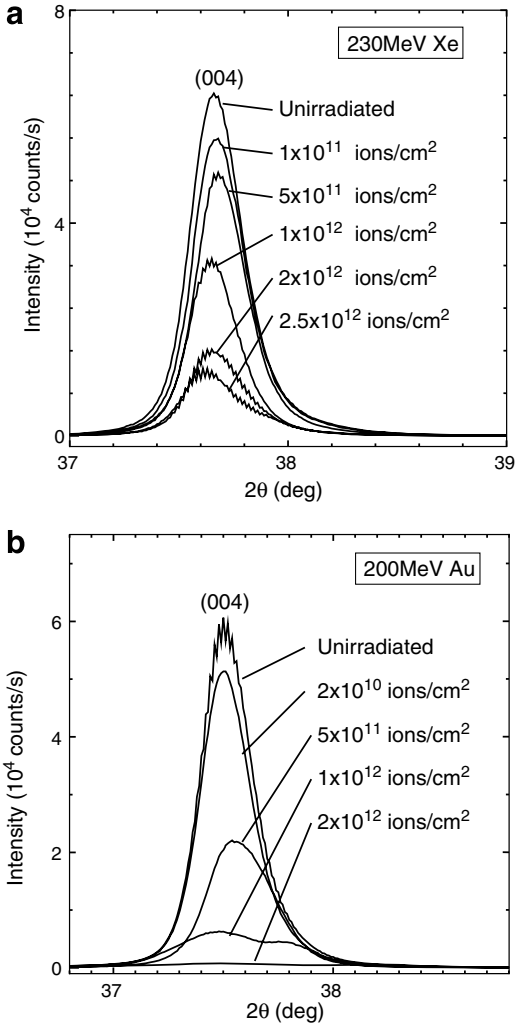

Fig. 2. Evolution of the XRD peak assigned to the (004) plane of anatase TiO_2 before and after irradiation with (a) 230-MeV Xe ions and (b) 200-MeV Au ions.