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Implantation of anatase thin film with 100 keV ^{56}Fe ions: Damage formation and magnetic behaviour

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ABSTRACT

We have investigated the damage morphology and magnetic properties of titanium dioxide thin films following implantation with Fe ions. The titanium dioxide films, having a polycrystalline anatase structure, were implanted with 100 keV $^{56}Fe^{+}$ ions to a total fluence of 1.3×10^{16} ions/cm^2. The ion bombardment leads to an amorphized surface with no indication of the presence of secondary phases or Fe clusters. The ion-beam induced damage manifested itself by a marked change in surface morphology and film thickness. A room temperature ferromagnetic behaviour was observed by SQUID in the implanted sample. It is believed that the ion-beam induced damage and defects in the polycrystalline anatase film were partly responsible for the observed magnetic response.

1. Introduction

Titanium dioxide (TiO_2) is a very interesting and versatile material with a wide range of applications, including use in microelectronics due to its high dielectric constant and in optical coatings due to its high refractive index. It also has excellent optical transmittance in the visible and near-infrared region and is a wide band gap semiconductor. These are very suitable characteristics for electronic and optical applications [1]. In addition, the induced magnetic properties when doped with magnetic impurities e.g. Fe may give rise to a suitable magnetic oxide. Such ferromagnetic semiconductors are of great interest due to their potential application for future spintronics devices [2]. Transparent ferromagnetic semiconductors are appealing materials for magnetooptical devices [3]. Contradictory theoretical and experimental results have been obtained following doping of TiO_2 [4]. It is not even certain if the ferromagnetic response, which was found in some cases, is due to defects inside TiO_2 or originates from nanoscale precipitates or other induced magnetic phases. Much attention has been given to Co:TiO_2 where a ferromagnetic response was demonstrated [3], although, magnetic response mechanisms in Fe:TiO_2 are still under discussion [5]. The magnetic properties of doped TiO_2 show a dependence on the different phases (rutile, anatase or amorphous), the type (bulk or thin film) and its composition.

In addition to interesting magnetic properties, doped anatase-type TiO_2 is an extensively studied photo-catalytic semiconductor [6,7]. Doping of TiO_2 with Fe has been shown to enhance the efficiency of its photoactivity [7,8], although its role concerning the electron-hole recombination process is not fully understood [9].

Many deposition techniques are used for TiO_2 synthesis, although magnetron sputtering remains the preferred method especially for large area coatings [10]. This is due to the process versatility, uniformity, ease of scaling-up and high throughput. For technological applications it is often necessary to fabricate well-ordered micro- or nano-structures [11], with periodic variations in refractive index for photonics components, in magnetic properties, or in active catalytic surface areas. One method of

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fabricating regular nano- and micro-structures is by ion beam-based projection lithography [11,12], where the pattern is defined by a mask. Ion implantation is a well-known materials engineering process by which dopants are introduced into a material and induce high contrast material modifications.

In this work we have studied the behaviour of polycrystalline TiO_2 anatase thin films following ion implantation and its consequences for tailoring nano-and micro-structures. The samples were prepared by reactive magnetron sputter deposition, and implanted at room temperature with 100 keV $^{56}Fe^+$ ions.

2. Experimental details

The deposition setup and process are described in detail elsewhere [13,14]. The thin films were grown by reactive magnetron sputtering in an argon/oxygen atmosphere using a Von Ardenne reactive balanced magnetron sputter deposition system operated in a pulsed direct current (DC) mode. A constant power mode of 800 W at a frequency of 20 kHz was applied. The titanium sputter target was mounted 45° off-axis and at a distance of about 100 mm from the substrates. The base pressure in the system was below 2×10^{-7} Torr, while the working pressure was held constant at 4.0 mTorr. The flows of argon and oxygen were 50 and 13 sccm, respectively. The films were deposited onto silicon (100) wafers. During deposition the substrate was heated to 300 °C using a front side radiation heater. The deposition resulted in a polycrystalline anatase film with a thickness of 475 ± 25 nm as measured by cross-sectional SEM.

Samples of 1×1 cm^2 were implanted with 100 keV $^{56}Fe^+$ ions at room temperature under normal incidence to a total fluence of 1.3×10^{16} ions/cm^2. The average scanned ion beam flux was kept constant at about 7×10^{11} cm^{-2} s^{-1}. A single sample was implanted through a copper TEM grid with an array of 10×10 μm^2 square openings.

The compositions of the as-deposited and implanted films were measured by Rutherford Backscattering Spectrometry (RBS) [15] using a 3.0 MeV He^+ ion beam backscattered into a detector at 167° relative to the incident beam direction. In addition Time-of-Flight elastic recoil detection analysis (ToF-ERDA) [16] using a 40 MeV $^{127}I^{9+}$ ion beam was performed to give the relative elemental concentration profile. A detailed description of the experimental set-up has been given elsewhere [17].

Structural analysis of the films was performed by means of grazing incidence (0.5°) X-ray diffraction measurements using Cu $K_{\alpha 1}$ (1.5604 Å) radiation. A LEO 1550 FEG high resolution scanning electron microscope (SEM) was used to investigate the surface morphology of as-deposited and implanted samples. Atomic force microscopy (AFM), magnetic force microscopy (MFM), and optical microscopy was done on the sample implanted through the copper TEM grid. The AFM was performed in non-contact mode using a PSIA XE150, and the MFM measurement was carried out using a Cervantes from Nanotec and Nanosensor HM tips.

Finally, magnetic measurements were performed on the as-deposited and implanted samples, using a Superconducting Quantum Interference Device (SQUID) at 4 and 300 K. The external magnetic field was applied in-plane.

3. Results and discussions

The XRD measurements of the as-deposited sample revealed a polycrystalline anatase structure, see Fig. 1. There is a preferential growth of the (211) anatase crystal plane. After implantation the film loses part of its crystallinity as the diffraction peaks reduce in intensity and even disappear for some crystal planes. For the implanted samples, there were no signals in the XRD diffractograms to indicate the formation of Fe clusters or other oxide phases, nor was any phase change detected [18].

A RBS spectrum obtained from the as-deposited film is shown in Fig. 2(a). The RBS analysis shows that the film is sub-stoichiometric in oxygen, giving a ratio between O and Ti of 1.9. This was confirmed by the ERDA measurements. Furthermore, as the RBS and ERDA measurements give the areal density of atoms in the films, the mass density of the deposited film could be estimated. Using the mean physical thickness of 475 nm an average value of 3.15 g/cm^3 for the density was obtained. It should be noted that

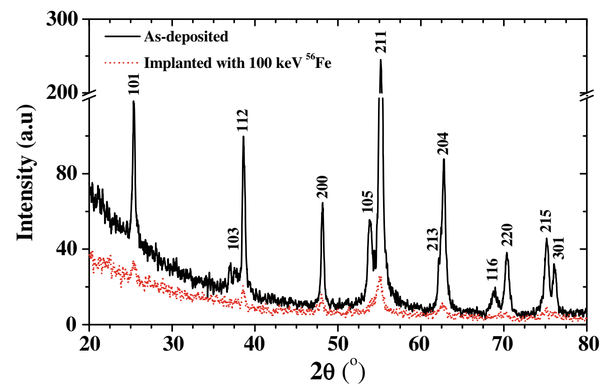

Fig. 1. Grazing incidence X-ray diffractograms of the as-deposited anatase polycrystalline film (solid curve), and the sample implanted with 100 keV $^{56}Fe^+$ ions to a fluence of 1.3×10^{16} ions/cm^2 (dotted line). The diffraction planes belonging to the TiO_2 anatase phase are indicated. Note the break on the ordinate axis.

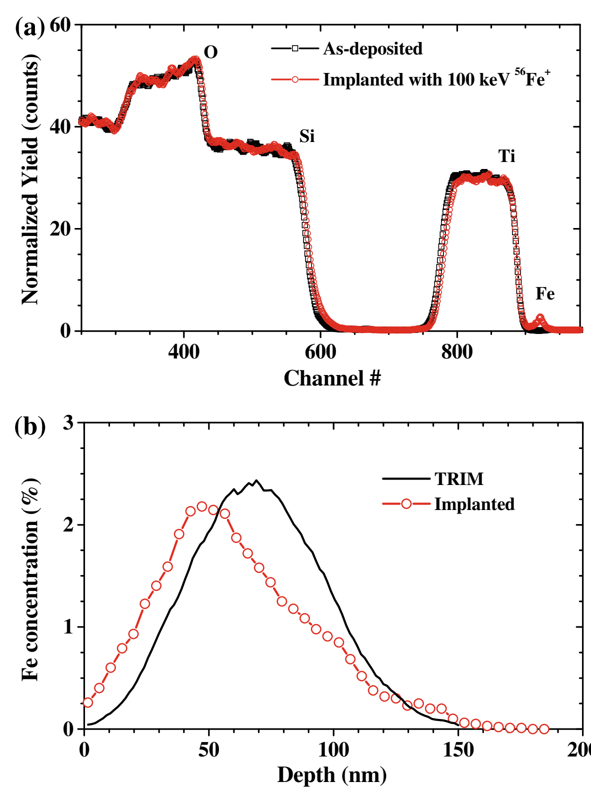

Fig. 2. (a) RBS spectra of the as-deposited thin film and after implantation with 100 keV $^{56}Fe^+$ ions to a fluence of 1.3×10^{16} ions/cm^2. The increase in the oxygen signal towards the surface is due to a resonance in the scattering cross section for ^4He incident on oxygen. (b) Fe implantation profile simulated by TRIM [22] (solid curve), and the Fe distribution in the implanted sample as measured by ToF-ERDA. In both cases the estimated average density of the deposited film was used to obtain the Fe depth profiles.