Proton irradiation of TiO_2 rutile single crystals

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INTRODUCTION

The aim of the experiment was to study the influence of ion irradiation on the optical properties of TiO_2 in rutile phase, to foresee future possible applications in the activation of resistive switching effect for memristor fabrication by ion beam lithography. The scientific literature is plentiful of evidences highlighting how the properties of electronic devices based on TiO_2 can be improved through electronic doping or simply by radiation hardening [1,2]. In this wide pool of works, the ones dedicated to the memristor technology cover a key role in the development of the next-generation memories alternative to the silicon technology. A memristor cells is constituted by an active layer of insulating material embodied between two conductive electrodes. In its virgin state the cell is insulating, and through a voltage-driven step, the so-called electroforming, the formation of defects, acting as filamentary conductive paths for the current, is promoted in the matrix. In memristor cell composed by oxides of transition elements, the increased conductivity is commonly described as mix between ionic and electronic contributions. A redox-based mechanism takes place inside the active layer, in which the created oxygen vacancies reduce the valence of the metal and enhance the ionic conductivity of the matrix [3].

In this scenario, the control of the matrix properties through the creation of different type of defects, (displacement, substitutional and structural) is of paramount importance for the cell functioning. A valid way to explore this topic in its different nuances can rely on the use of ion irradiation. In fact, ions can be exploited in different extent not only to introduce structural disorder but also to create ion-specific defects. To the best of our knowledge, few studies can be found on this more specific topic, especially for bulk single crystals. For example, implanting different ions (Sn, Au, Sb, W, Hg, In, Hf, and La) in rutile single crystals, Meyer et al. [4] monitored the defect formation through Rutherford Backscattering Spectroscopy and electrical conductivity measurements. An enhancement of the electrical conductivity has been found and attributed to the formation of point defects rather than to the ionic doping introduced by the implanted ionic species. A more important focus on the accumulation of structural defects introduced by ion irradiation, have been given by Harmann et al. [5], which by studying the radiation damage effects induced by irradiation of rutile with noble gas ions of increasing size (He^+, Ne^+ and Xe^{2+}), have demonstrated how the structural and mechanical properties of TiO_2 are more sensitive to the point defects accumulation introduced by the lightest He^+ ion, rather than to the formation of extended defects for the collision cascades of the heavier ions. An opening toward defects engineering in TiO_2 nanotubes by means of ion irradiation comes from Liu at al., who showed how irradiating with H^+ at high energies can generate defects similar to the ones observed in “black titania” [6]. In this material, the boost in electrical conductivity and light absorption properties are believed to ensue from the presence of Ti^{3+} colour centers [7]. The same type of centers has also been created by ion sputtering on rutile TiO_2 single crystals surface [8]. In the same study the formation of a superficial Ti^{3+} rich layer has been demonstrated to promote the growth of nanodots structures.

Following the present evidences, the irradiation with the light H^+ ions, enabling both the reduction of the Ti^{4+} cations and the creation of ionization defects in a cumulative way, represents a good starting point to lay the groundwork for a systematic study on the tailoring of the properties of TiO_2 bulk crystal by means of ion irradiation. This first attempt will be here investigated by means of ionoluminescence monitored systematically at increasing ion fluence implantation.

EXPERIMENTAL METHOD

The samples under exam are single crystals of TiO_2 in rutile phase produced by CRYSTAL GmbH. The $10\times10\times0.5$ mm^3 samples are cut along the [110] crystal direction and optically polished on one single face.

The simulations of the depth profile of the damage density, evaluated in first approximation as the product between the linear damage density (number of vacancies per unit length per incoming ion) and the implantation fluence (number of implanted ions per unit surface), were performed with SRIM Monte Carlo numerical simulations. The numerical Monte Carlo code employed is “Stopping and Range of Ions in Matter” (SRIM), in its 2013.00 version. In the simulation, the “detailed calculation with full damage cascade” mode was adopted, while taking the atom displacement energy values of 28 eV for oxygen and 25 eV for titanium and considering a mass density of 4.23 g cm^{-3}.

Ionoluminescence spectra were simultaneously acquired during irradiations. The adopted set-up consists of a collecting lens placed inside the chamber and connected to a QRPro Ocean Optics cooled spectrometer through optical-fibres. Each spectrum was obtained as the average of two different acquisitions and setting an integration time of 10 s.

Ion irradiations were performed using 600 keV protons beam with a spot size of 1.4×1.8 mm^2 and 2 MeV protons beam with a spot of 0.4 × 0.5 mm^2, in both cases the current was around 0.8 nA. The scattering line used was the 0° since was recently equipped with a charge suppressor ensuring an accurate measure of the beam current and therefore the implantation fluence evaluation, a crucial parameter for this experiment. This element is a cylindrical electrode surrounding the sample holder and biased at -400 V, properly designed to suppress the secondary electrons ejected from the sample.

RESULT AND DISCUSSION

The effect of ion irradiation on the crystal lattice and optical properties of the TiO_2 sample has been indirectly investigated by monitoring the changes in ionoluminescence intensity. As visible in Figure 1A, the samples show the typical rutile NIR emission, likely involving a deep midgap state [9], centered at about 830 nm. Considering 2 MeV protons, an increase of the fluence from 5 × 10^{13} cm^{-2} to 8 × 10^{14} cm^{-2} leads a progressive decrease of the band intensity of about 6 times. This phenomenon can have a twofold explanation: (i) we are inducing a progressive amorphization of the sample, destroying the sites associated to the IL emission; (ii) we are considerably increasing the number of oxygen vacancies (see SRIM simulation in Figure 1B), inducing a partial reduction of the sample, which has been reported to be associated with a reduced intensity in the observed luminescence [9].

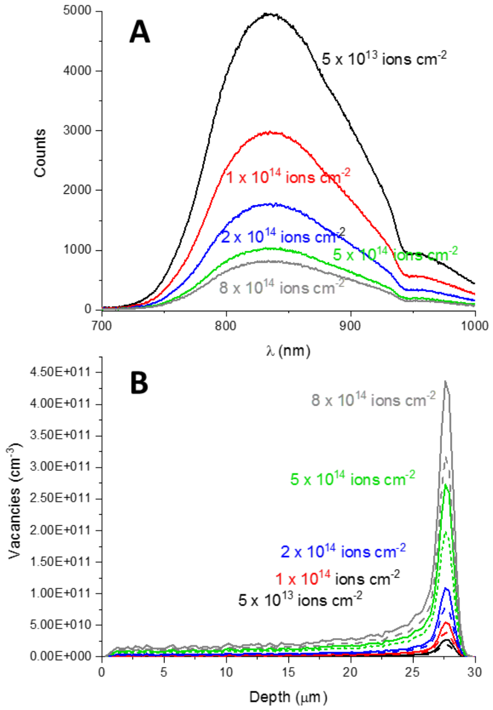

Figure 1. A. Ionoluminescence spectra of the TiO2 sample irradiated with 2 MeV protons at increasing fluences. B. Depth profile of the atomic vacancies (solid lines: O atoms, dashed lines: Ti atoms) generated by the ion beam.

Moving now to 600 keV protons, from Figure 2A we can observe that, at comparable fluences, the IL intensity is considerably lower with respect to the corresponding spectra acquired with 2 MeV protons. This can be explained by the lower penetration depth of 600 keV protons: the Bragg peak is located about 4.5 μm from the surface (Figure 2B). This induces a higher density of vacancies (Figure 2B) at the same fluence in the irradiated volume, enhancing the effects previously described.

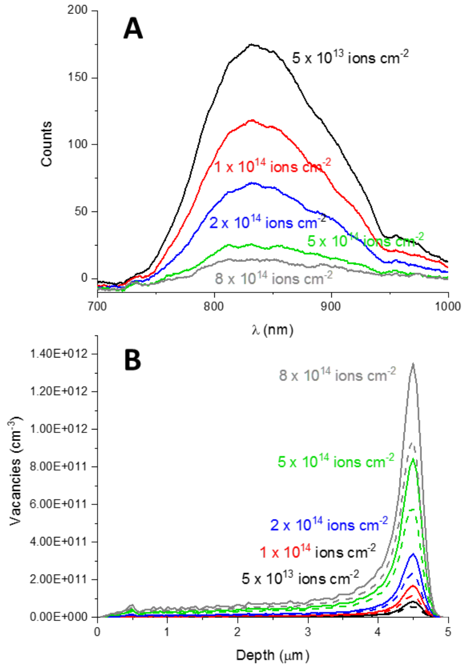

Figure 2. A. Ionoluminescence spectra of the TiO2 sample irradiated with 600 keV protons at increasing fluences. B. Depth profile of the atomic vacancies (solid lines: O atoms, dashed lines: Ti atoms) generated by the ion beam.

CONCLUSIONS

In this report, we presented a systematic investigation on the ionoluminescence variation after proton beam irradiation of TiO_2 rutile at two different energies over a range of fluence from 5 × 10^{13} cm^{-3} up to 8 × 10^{14} cm^{-3}.

Further investigations are needed in order to identify the defects involved in the observed effects, performing also an experiment using He ion beam. Moreover, a monitoring of the electrical properties variation simultaneously to the irradiations is foreseen to better explore the possible activation of resistive switching effect for memristor fabrication by ion beam lithography.

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