

Proton irradiation of TiO₂ 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 TiO₂ 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 TiO₂ 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 Xe²⁺), have demonstrated how the structural and mechanical properties of TiO₂ 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 TiO₂ nanotubes by means of ion irradiation comes from Liu et 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 Ti³⁺ colour centers [7]. The same type of centers has also been created by ion sputtering on rutile TiO₂ single crystals surface [8]. In the same study the formation of a superficial Ti³⁺ 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 Ti⁴⁺ 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 TiO₂ 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 TiO₂ in rutile phase produced by CRYSTAL GmbH. The 10×10×0.5 mm³ 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 mm² and 2 MeV protons