

## Functional Modifications Induced via X-ray Nanopatterning in TiO<sub>2</sub> Rutile Single Crystals

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The possibility to directly write electrically conducting channels in a desired position in rutile  $TiO_2$  devices equipped with asymmetric electrodes—like in memristive devices—by means of the X-ray nanopatterning (XNP) technique (i.e., intense, localized irradiation exploiting an X-ray nanobeam) is investigated. Device characterization is carried out by means of a multitechnique approach involving X-ray fluorescence (XRF), X-ray excited optical luminescence (XEOL), electrical transport, and atomic force microscopy (AFM) techniques. It is shown that the device conductivity increases and the rectifying effect of the Pt/TiO<sub>2</sub> Schottky barrier decreases after irradiation with doses of the order of  $10^{11}$  Gy and fluences of the order of  $10^{12}$  J m<sup>-2</sup>. Irradiated regions also show the ability to pin and guide the electroforming process between the electrodes. Indications are that XNP should be able to promote the local formation of oxygen vacancies. This effect could lead to a more deterministic implementation of electroforming, being of interest for production of memristive devices.

## 1. Introduction

Silicon-based electronics has recorded an exponential decrease for decades about the sizes of its basic components to achieve larger and larger integration scales and keep the pace of the so-called Moore's law. Nowadays, approaching the 7 nm technological node, the unavoidable process fluctuations create new challenges and require more and more sophisticated and

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## DOI: 10.1002/pssr.202100409

expensive engineering solutions.<sup>[1]</sup> In this scenario, alternative approaches and novel device concepts are clearly desirable both to sustain further increase in the integration scale and to improve device functionality and performances. Oxide electronics has recently emerged as one of such promising approaches, having already been able to provide monolithic full-oxide integrated circuits, for instance.<sup>[2]</sup> But the advent of this new oxide-based technology has also opened the way to the fabrication of conceptually new devices like memristors,<sup>[3]</sup> i.e., resistive devices with inherent memory properties that previously existed just as theoretical models. Since then, memristor-based electronics has seen a rapid progress and showed great potential for many applications spanning from neuromorphic computing to on-chip memory and

storage.<sup>[4–6]</sup> These devices are typically based on the reversible change of the electrical properties of transition metal oxides upon the application of an electric field that causes the introduction and migration of oxygen vacancies, which act as mobile donors in these systems. The typical two-terminal device structure of memristors consists of a dielectric layer of a material like TiO<sub>2</sub>, SrTiO<sub>3</sub>, or HfO<sub>2</sub> placed between two metallic electrodes. Prior to the reversible operation of the devices, a voltage

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