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Tailoring the Local Conductivity of TiO_2 by X-Ray Nanobeam Irradiation

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It is well known that intense synchrotron beams can alter the state of materials, but this effect is generally considered undesired radiation damage. The effect of local irradiation of TiO_2 rutile single crystals is investigated by a 56×57 nm^2 synchrotron X-ray nanobeam at 17.4 keV. Aside from a transient increase of conductivity due to a photovoltaic-like process, a nonvolatile localized change of resistance by about 4 orders of magnitude is measured after X-ray exposure. This effect can be ascribed to the local generation of oxygen vacancies by the X-ray nanoprobe, which are subsequently ordered by the electric field applied during the acquisition of *I–V* curves. These results demonstrate that intense synchrotron beams can create oxygen vacancies in materials with tightly bound oxygen atoms, highlighting that X-ray nanoprobes could become an effective tool for oxide nanofabrication, able to locally tune the material resistivity. For instance, since the localized presence and migration of oxygen vacancies is an essential requisite for redox-based memristive devices, the possibility to locally induce oxygen vacancies could represent a novel tool for the production of oxide-based memristive devices, replacing the problematic electroforming step.

1. Introduction

It has long been known that intense synchrotron X-ray beams can alter the state of matter.[1] This issue has been widely studied in the field of soft matter and protein crystallography since radiation damage is a major concern in experiments involving these systems.[2] Inorganic hard condensed matter is generally much less sensitive to X-rays, nevertheless the recent remarkable improvements in both brilliance of synchrotron radiation sources and performance of X-ray focusing optics are pushing the power density on the sample to unprecedented values in nanobeam experiments,[3] making radiation damage also relevant for inorganic materials.[4] However, in the last years some studies suggested that this effect, which is generally undesired, could be exploited to modify materials in a controlled way. In this respect, a few interesting examples have been reported, including, for instance, redox reactions,[5] X-ray-induced crystallization,[6] metal–insulator[7] and structural phase transitions.[4a,8]

In the case of the nonstoichiometric superconducting oxides, Poccia et al.[9] showed that 12.4 keV X-rays can induce the ordering of interstitial O atoms and a change in the critical temperature of La_2CuO_{4+y}. Thereafter, our group highlighted that a high-dose irradiation at 17 keV can affect both structural and electronic properties of $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) microcrystals by modifying both their mosaicity and their oxygen content (i.e., displacing weakly bound interstitial O atoms and thus increasing the material resistivity).[10] Taking inspiration from these results, we have developed the idea of exploiting synchrotron radiation to directly write the geometry of an electrical device on the material without any additional step, like photoresist impression and subsequent etching, as done in conventional lithographic processes. This X-ray nanopatterning (XNP) process is based on the modification of the material oxygen content (and thus of its local electrical properties) induced by the X-ray nanobeam. Following this approach, we succeeded in fabricating a proof-of-concept Josephson device out of Bi-2212 without disrupting its crystal structure using XNP,[11] recently achieving a minimum feature size of 50 nm.[12]

On the other hand, a lot of efforts are presently being spent in the field of oxide electronics, where many full-oxide electronic components have already been fabricated, up to monolithically integrated circuits.[13] The typical patterning process used for these fabrications has been ordinary electron-beam or photolithography, borrowing the technology

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