Introduction

Lithographic methods lie at the heart of modern-day nanotechnology. Their development in the reduction of pattern motifs in functional materials has enabled the fabrication of high-performing and cost-effective integrated circuits, storage devices, displays, biosensors, DNA microarrays and advanced materials.1 The main improvements in the past few decades were mainly based on the decrease of the radiation wavelength, which has enabled a corresponding decrease of the minimum feature size, so that nowadays 193 nm ArF lasers represent the standard for high volume production. However, further decrease towards shorter wavelengths at the moment is limited only to research and development activities, mainly due to the lack of suitable laser sources or photoresists compliant with industrial standards. For instance, this is still the case for extreme ultraviolet (EUV) lithography exploiting $\lambda = 13.5$ nm, which is considered a good candidate for the sub-20 nm technological nodes and indeed has already shown the capability to produce patterns with resolutions down to 8 nm half-pitch in its interference version.2

A very different approach could be represented by the use of intense, highly-focused, hard X-ray beams to tailor the material growth and properties at the nanoscale. Indeed, X-rays produced by synchrotrons and free electron lasers have already proved to be able to stimulate the organized growth of nanostructures,3 to manipulate defects4 and to modify the properties of materials.5 From this point of view, the viability of an approach based on maskless X-ray nanopatterning has been recently demonstrated by Truccato et al. by fabricating a proof-of-concept electrical device out of the superconducting oxide Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi-2212).6 This patterning method represents a conceptual novelty because it does not imply any material removal from the substrate and is just based on the spatial modulation of the lattice electrical properties, with great potential advantages in terms of heat dissipation, chemical contamination and mechanical stability of the devices.

However, the full development of this patterning technique requires a good understanding of the underlying chemical-physical mechanisms that connect the X-ray exposure with the changes in the electric properties, in order to finely tune the desired modifications. The processes involved are expected to depend on the material absorption properties and on dis-excitation mechanisms, that in turn depend on the material composition and structure, the X-ray wavelength, irradiation dose and possibly from the X-ray flux and exposure time. Indeed, several mechanisms have been evoked so far in literature for material modifications induced by X-rays, including for instance sample heating, formation of

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Valentina Bonino, a Angelo Agostino, b Carmelo Prestipino, c Olivier Hernandez, c Matteo Fretto, d Lorenzo Mino b and Marco Truccato d

We have investigated the modifications induced in the high-$T_c$ superconductor Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi-2212) by X-ray nanopatterning, which is an innovative, photoresist-free, direct-writing approach recently used to fabricate proof-of-concept electrical devices [Truccato et al., Nano Lett., 2016, 16, 1669]. By means of combined synchrotron microdiffraction and electrical transport measurements carried out on the same Bi-2212 microcrystal, we show that hard X-ray irradiation with fluences of the order of $10^{12}$ J m$^{-2}$, corresponding to doses of the order of $10^{13}$ Gy, induces crystal fragmentation into multiple subdomains and decreases the carrier density of the system. We ascertain that the synergistic action of grain boundaries and of oxygen removal from the material dramatically changes the properties of Bi-2212 both in the normal and in the superconducting state. This special feature of X-ray nanopatterning introduces an opportunity that could be exploited to finely tune material structural defects according to the desired properties.

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1 Department of Physics, Interdepartmental Centre NIS, University of Torino, via P. Giuria 1, I-10125 Torino, Italy. E-mail: marco.truccato@unito.it
2 Department of Chemistry, Interdepartmental Centre NIS and INSTM Centro di Riferimento, University of Torino, via P. Giuria 7, I-10125 Torino, Italy
3 University of Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) - UMR 6226, F-35000 Rennes, France
4 Nanofacility Piemonte INRIM (Istituto Nazionale di Ricerca Metrologica), Strada delle Cacce 91, 10135, Torino, Italy
5 Electronic supplementary information (ESI) available. See DOI: 10.1039/c8ce01183d

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