

PAPER

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Creation of pure non-crystalline diamond nanostructures *via* room-temperature ion irradiation and subsequent thermal annealing

F. Picollo,^a A. Battiato,^b F. Bosia,^{a,c} F. Scaffidi Muta,^a P. Olivero,^{a,b} V. Rigato^d and S. Rubanov^e

Carbon exhibits a remarkable range of structural forms, due to the availability of sp^3 , sp^2 and sp^1 chemical bonds. Contrarily to other group IV elements such as silicon and germanium, the formation of an amorphous phase based exclusively on sp^3 bonds is extremely challenging due to the strongly favored formation of graphitic-like structures at room temperature and pressure. As such, the formation of a fully sp^3 -bonded carbon phase requires an extremely careful (and largely unexplored) definition of the pressure and temperature across the phase diagram. Here, we report on the possibility of creating full- sp^3 amorphous nanostructures within the bulk crystal of diamond with room-temperature ion-beam irradiation, followed by an annealing process that does not involve the application of any external mechanical pressure. As confirmed by numerical simulations, the (previously unreported) radiation-damage-induced formation of an amorphous sp^2 -free phase in diamond is determined by the buildup of extremely high internal stresses from the surrounding lattice, which (in the case of nanometer-scale regions) fully prevent the graphitization process. Besides the relevance of understanding the formation of exotic carbon phases, the use of focused/collimated ion beams discloses appealing perspectives for the direct fabrication of such nanostructures in complex three-dimensional geometries.

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1. Introduction

Carbon is an extremely “versatile” chemical element due to the availability of different types of hybridized chemical bonds (sp^1 , sp^2 and sp^3), that determine a remarkable range of possible allotropic forms, both in bulk form and as nanostructures.¹ In many respects, diamond lies at the very extreme of such a range, as far as bulk structures are concerned: due to its strong covalent sp^3 bond, the diamond crystal is characterized by extreme mechanical (high hardness, low friction coefficient), optical (broad transparency from the near UV to the far IR), thermal (large thermal conductivity, low thermal expansion coefficient) and electrical (extreme dielectric strength, high carrier mobility) properties.² These unique characteristics have motivated a remarkable body of scientific work aimed at better understanding its fundamental properties, as well as its synthesis and

application in many different technological fields, ranging from high-power to quantum devices, encompassing biosensors, MEMS technology and much more.^{3–5} Not only has the systematic production of high-quality artificial diamond crystals *via* high-pressure-high-temperature (HPHT)⁶ and chemical-vapor-deposition (CVD)⁷ techniques made remarkable progress in the past decades, but the development of devices based on micro- and nano-crystalline diamond has also attracted ever-increasing interest, thanks to the fact that several appealing characteristics (most remarkably mechanical ones) are largely preserved in a material platform requiring less sophisticated synthesis methods.⁸

Moving towards more “defective” and technologically viable forms of sp^3 -bonded carbon, different forms of polycrystalline diamond,⁹ ultra-nanocrystalline diamond,¹⁰ nano-twinned diamond¹¹ and amorphous diamond-like carbon^{12,13} have been widely investigated for several decades, with the promise of further expanding the applicability of extreme physical properties into technological landscapes in which synthesis and fabrication techniques can be realistically scaled to large production volumes. In this context, the higher thermodynamical stability of sp^2 -bonded carbon at room pressure and temperature conditions represents a fundamental limitation: in these conditions, graphite and graphite-like phases constitute the ultimate “ground state” for carbon structures when a critical amount of structural disorder is introduced. For this reason,

^aPhysics Department and “NIS Inter-departmental Centre”, University of Torino, Torino 10125, Italy. E-mail: paolo.olivero@unito.it

^bNational Institute of Nuclear Physics, Section of Torino, Torino 10125, Italy

^cApplied Science and Technology Department, Politecnico di Torino, Torino 10129, Italy

^dNational Institute of Nuclear Physics, National Laboratories of Legnaro, Legnaro 35020, Italy

^eIan Holmes Imaging Centre, Bio21 Institute, University of Melbourne, Victoria 3010, Australia