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

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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.



31 1. Introduction

32 Carbon is an extremely “versatile” chemical element due to the availability of different types
33 of hybridized chemical bonds (sp^1 , sp^2 and sp^3), that determine a remarkable range of
34 possible allotropic forms, both in bulk form and as nanostructures [1]. In many respects,
35 diamond lies at the very extreme of such a range, as far as bulk structures are concerned: due
36 to its strong covalent sp^3 bond, the diamond crystal is characterized by extreme mechanical
37 (high hardness, low friction coefficient), optical (broad transparency from the near UV to the
38 far IR), thermal (large thermal conductivity, low thermal expansion coefficient) and electrical
39 (extreme dielectric strength, high carrier mobility) properties [2]. These unique characteristics
40 have motivated a remarkable body of scientific work aimed at better understanding its
41 fundamental properties, as well as its synthesis and application in many different
42 technological fields, ranging from high-power to quantum devices, encompassing biosensors,
43 MEMS technology and much more [3-5]. Not only has the systematic production of
44 high-quality artificial diamond crystals via high-pressure-high-temperature (HPHT) [6] and
45 chemical-vapor-deposition (CVD) [7] techniques made remarkable progress in the past
46 decades, but the development of devices based on micro- and nano-crystalline diamond has
47 also attracted ever-increasing interest, thanks to the fact that several appealing characteristics
48 (most remarkably mechanical ones) are largely preserved in a material platform requiring less
49 sophisticated synthesis methods [8].

50 Moving towards more “defective” and technologically viable forms of sp^3 -bonded carbon,
51 different forms of polycrystalline diamond [9], ultra-nanocrystalline diamond [10],
52 nano-twinned diamond [11] and amorphous diamond-like carbon [12, 13] have been widely
53 investigated for several decades, with the promise of further expanding the applicability of
54 extreme physical properties into technological landscapes in which synthesis and fabrication
55 techniques can be realistically scaled to large production volumes. In this context, the higher
56 thermodynamical stability of sp^2 -bonded carbon at room pressure and temperature conditions
57 represents a fundamental limitation: in these conditions, graphite and graphite-like phases
58 constitute the ultimate “ground state” for carbon structures when a critical amount of
59 structural disorder is introduced. For this reason, substantial efforts have been made in the
60 synthesis of amorphous carbon phases characterized by a high fraction of sp^3 bonds [14-16],
61 but the pursuit of a 100% fully sp^3 -bond amorphous carbon phase is still ongoing. A careful
62 control of environmental parameters (pressure in particular) allows the engineering of novel
63 forms of carbon, as demonstrated by the fact that exerting high (i.e. $\sim 10^2$ GPa) pressures on



64 glassy carbon (i.e. an amorphous sp^2 phase) yields the formation of phases characterized by
65 high sp^3 content with no long-range ordering, whose structural stability can to some extent be
66 tuned if an equally careful control of temperature variable can be achieved [17-19]. In this
67 context, a powerful and versatile tool is represented by the local laser heating of different
68 types of carbon structures under different mechanical stress conditions, either exerted from
69 external pressure sources [20] or established within the sample by the coexistence of carbon
70 phases characterized by different densities and mechanical properties [21].

71 Local laser heating was combined with the possibility offered by MeV ion irradiation to
72 create sub-superficial graphitic structures within bulk diamond thanks to the strongly
73 non-linear damage profile of energetic ions in matter. The ion-damage-induced collapse into
74 a graphitic phase of layers with sub- μm thickness localized within the diamond crystal
75 determines substantial local variations in both atomic density and mechanical parameters
76 (Young's and shear moduli), that can in turn develop strong (i.e. ~ 10 GPa) and highly
77 localized internal stresses, without the need of using external pressure sources [22]. In these
78 conditions, optical absorption of the laser light at different power densities from the
79 sub-superficial compressed graphitic layers allowed a fine control of local temperature
80 variations, and thus an accurate exploration of the graphite-diamond-liquid triple point [23].
81 In this context, the employment of other types of radiation (e.g. x-ray nano-beams) could be
82 successfully employed to engineer structural damage with high spatial resolution, as already
83 successfully demonstrated in other types of substrates [24-26].

84 More recently, a careful control of the *in situ* laser-induced heating of glassy carbon kept at
85 high (i.e. ~ 50 GPa) pressure by means of a diamond anvil cell allowed the exploration of a
86 very specific (and up to then scarcely studied) portion of the phase diagram of carbon, which
87 resulted in the first demonstration of the synthesis of quenchable fully- sp^3 bonded amorphous
88 carbon phase. This stable amorphous phase of carbon was unequivocally demonstrated to be
89 based on a sp^2 -free structure by means of high-resolution transmission electron microscopy
90 (HRTEM) and electron energy loss spectroscopy (EELS), and exhibited properties of optical
91 transparency, high density and extreme stiffness that were comparable to those of diamond
92 [20].

93 In the present work, we take advantage of a high-resolution lithographic technique based on
94 the use of masked MeV ions to define sub-superficial amorphous nanostructures in the
95 diamond bulk induced by atomic collisions. We demonstrate by means of HRTEM and EELS
96 that these structures are lacking any measurable fraction of sp^2 bonds, specifically because



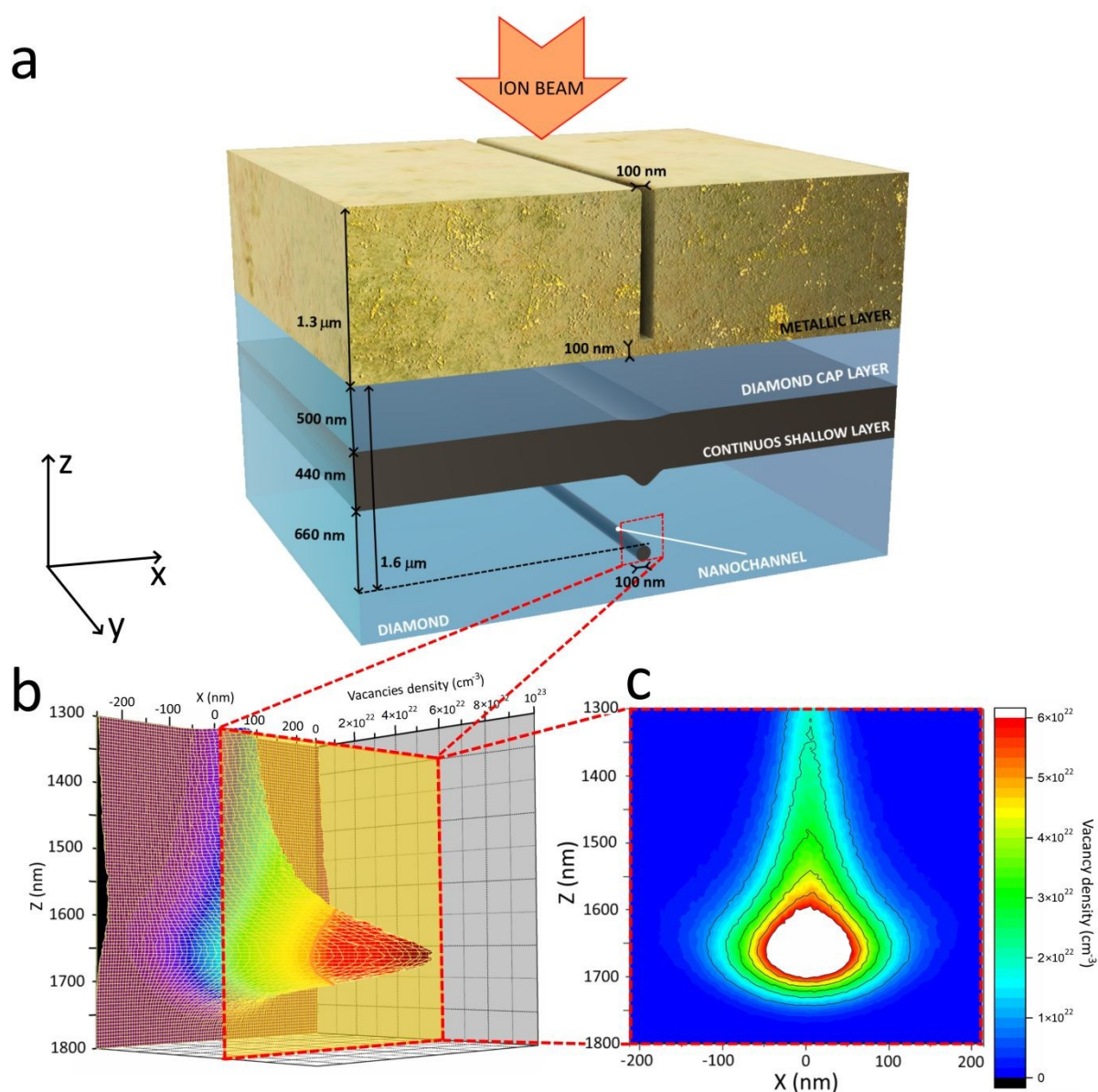
97 their size (i.e. ~100-200 nm, depending upon fabrication parameters) and depth below the
98 crystal surface (i.e. ~1.6 μm) is such to inhibit any form of graphitization by the development
99 of strong (i.e. >40 GPa) internal pressures. These results demonstrate for the first time the
100 possibility of direct MeV-ion-beam writing with high spatial resolution a quenchable
101 amorphous phase in diamond at room conditions, with no need of externally applied
102 pressures.

104 2. Results and discussion

105 Radiation-hard contact masks were lithographically defined at high spatial resolution on
106 single-crystal diamond samples, with the purpose of allowing ion irradiation across
107 nanometer-sized regions. To achieve this, focused ion beam (FIB) micromachining was
108 performed on a ~1.3 μm thick Copper layer deposited on the sample surface, resulting in the
109 formation of linearly shaped nano-apertures with 100 nm lateral width, as schematically
110 shown in Fig. 1. Notice that across the FIB-micromachined apertures the sample surface was
111 not fully exposed, but rather a ~100 nm thick metal layer was left at the bottom of the
112 aperture to avoid the contamination of the diamond surface with the milling Ga^+ ion beam.
113 After mask preparation, the samples were irradiated with a 1 MeV He^+ ion beam at
114 $5 \times 10^{16} \text{ cm}^{-2}$ fluence. As schematically shown in the inset plot of Fig. 1, the energy and
115 fluence of implanted ions was such that across the exposed areas a sub-superficial highly-
116 damaged layer was formed in correspondence of the end-of-range “Bragg peak” of the ion
117 damage profile, i.e. ~1.6 μm . Conversely, the irradiation occurring just below the masked
118 regions resulted in the formation of a shallow (i.e. ~500 nm) damaged region. Overall, as
119 schematically shown in Fig. 1a (and experimentally highlighted in Fig. 4a), ion-induced
120 structural damage resulted in the formation of sub-superficial narrow regions (referred to as
121 “nanochannels” in the following) located below an extended shallow region (referred as
122 “continuous shallow layer” in the following). The ~500 nm thick layer of diamond comprised
123 between the continuous shallow layer and the sample surface will be referred as “cap layer”
124 in the following. The mask thickness was specifically chosen to allow the formation of the
125 continuous shallow layer, that acted as the “reference” damaged region with respect to the
126 nanochannels. The main difference between these two types of structures consists in the
127 depth at which they are formed, since they are created upon the same irradiation carried over
128 the very same time.



129 After MeV ion irradiation and subsequent mask removal, the samples were thermally
 130 annealed in vacuum at 950 °C, with the scope of allowing the structural reorganization of the
 131 highly damaged buried nano-regions, while removing residual damage from the regions
 132 irradiated at intermediate depths.



133
 134 **Fig. 1** Sample geometry and profile of the ion-induced structural damage. **a** Schematic representation of the
 135 sample geometry: the metallic mask with the nanometric aperture determines the formation of both the
 136 continuous shallow layer and of the nanochannel upon MeV ion irradiation. **b** Three-dimensional plot of the
 137 cross-sectional profile of ion-induced damage density as resulting from SRIM simulation. **c** Corresponding
 138 two-dimensional plot: the size and shape of the region damaged beyond the estimated critical threshold (in red)
 139 corresponds to the features observed in Fig. 4a; note that the same plot is reported as an inset of Fig. 4a for
 140 sake of comparison with experimental data.

141



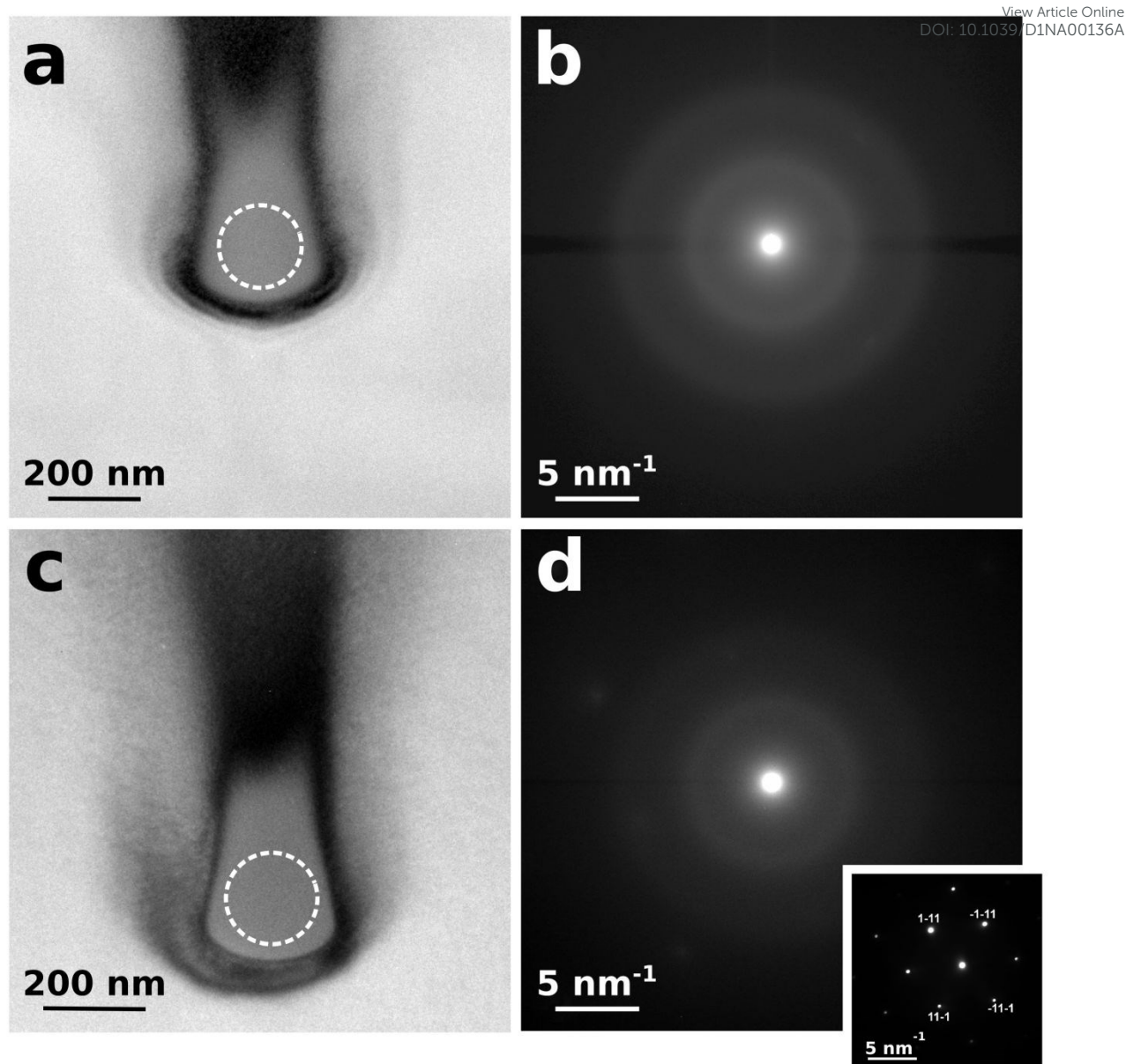
142 The nanochannels of highly-damaged carbon phase are expected to form where the structural
143 damage (here parameterized as a volume density of created vacancies, as predicted by the
144 SRIM Monte Carlo simulation code [27] in a linear approximation) exceeds a critical
145 threshold, whose value has been estimated as $\sim(6.4 \pm 1.5) \times 10^{22} \text{ cm}^{-3}$ on the basis of the
146 measured dimensions of the nanostructures (see Figs. 1b-c and Fig. 4a).

147 This value is in good agreement with previous estimations of the parameter, commonly
148 referred to as “graphitization threshold”, in the $(5-7) \times 10^{22} \text{ cm}^{-3}$ range [28-32]. As shown in
149 Fig. 1 (as well as in the inset of Fig. 4a), the SRIM-based model of the damage profile (which
150 also suitably describes the trajectories of laterally straggled ions) accurately predicts not only
151 the $\sim 1.6 \mu\text{m}$ depth of the nanochannels below the surface, but also their overall shape.

152 As shown in Figs. 2a and 2b, the bright-field TEM cross-sectional micrograph and related
153 selected area diffraction pattern indicate that the as-irradiated microstructures consist of a
154 fully amorphized phase. Remarkably, the same is observed also after the annealing step (see
155 Figs. 2c and 2d), thus indicating that the thermal process stabilizes the structures without
156 inducing any re-crystallization of either sp^2 or sp^3 phases. Dark contours are also visible
157 around the nanostructures, indicating lattice strains due to a high local concentration of point
158 defects. The diffraction patterns in Figs. 2b and 2d only show broad rings that are typical of
159 amorphous structures. It is worth remarking that the radius of the first ring correlates with the
160 positions of the $\{111\}$ diffraction spots generated from the surrounding crystalline diamond
161 matrix, as reported in the reference diffraction pattern reported in the inset of Fig. 2. This
162 confirms that the probed phase is fully amorphized. The absence in the diffraction patterns of
163 features related to sp^2 bonding (i.e. rings corresponding to the $\{002\}$ lattice plane of graphite)
164 can be attributed to a low fraction of sp^2 bonds or to a predominant orientation of graphite
165 basal plains normal to the electron beam direction.

166 In order to provide direct insight into the nature of the chemical bonds within the amorphized
167 nano-regions, EELS analysis was carried both before and after thermal annealing, in the
168 energy ranges corresponding to the K absorption edge of carbon and the plasmonic energy
169 loss. As far as the former energy range is concerned (see Fig. 3a), the K-edge EELS spectra
170 acquired from the nanostructure before thermal annealing are entirely lacking the articulated
171 post-edge structures observed in the corresponding spectra acquired from the surrounding
172 diamond matrix. Remarkably, this clear distinction in EELS spectral features is fully
173 preserved after the annealing step, thus indicating that no phases attributable to crystalline
174 diamond can be detected upon thermal processing.



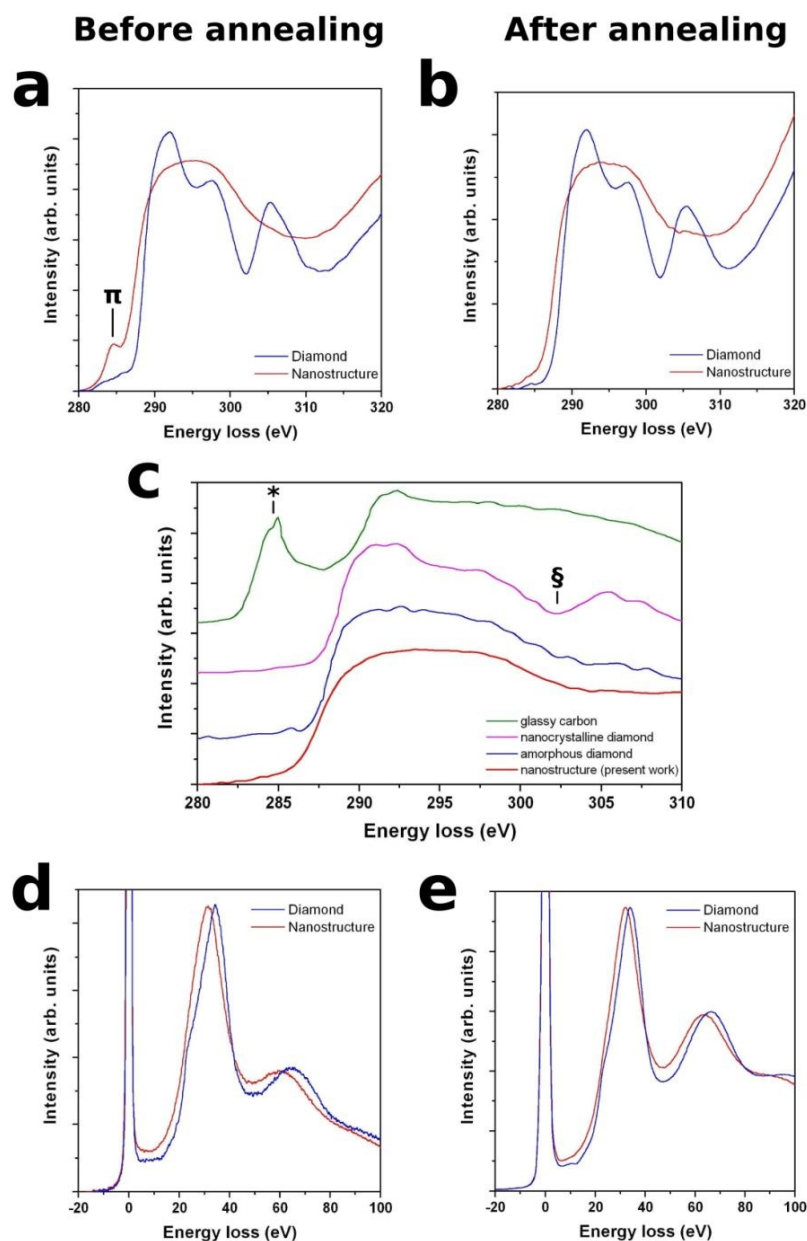


175
176 **Fig. 2** Results of cross-sectional TEM characterization of a nanostructure. **a** Bright-field TEM micrograph from
177 the as-implanted structure and **b** corresponding diffraction pattern collected from the area highlighted by the
178 dashed circle in **a**. **c** Bright-field TEM micrograph from the same structure after thermal annealing and **d**
179 corresponding diffraction pattern collected from the area highlighted by the dashed circle in **c**. A diffraction
180 pattern from the surrounding diamond matrix is reported in the inset for reference purpose.

181
182 Note that the spectra acquired from the nanostructures before thermal treatment exhibit a
183 well-defined (although not particularly intense) absorption pre-edge peak at ~ 285 eV that is
184 unequivocally attributed to π -bonded carbon [33], thus indicating that a fraction of sp^2 bonds
185 is indeed present in the as-implanted phase. Contrarily to what is commonly observed in
186 amorphized carbon, this spectral feature does not increase upon thermal annealing, but rather



187 completely disappears, which unequivocally indicates that the sp^2 bonds are absent from the
 188 annealed nanostructure within the detection limit of this very sensitive technique.



189
 190 **Fig. 3** Results of cross-sectional EELS spectroscopy of the nanostructures. K-edge absorption features of both
 191 the nanostructure (red plots) and the surrounding diamond matrix (blue plots) are reported for both the as-
 192 implanted (a) and thermally processed (b) sample. The pre-edge peak at ~ 285 eV, which is attributed to
 193 π -bonded carbon, is visible in a, while it is entirely absent in b. c Present experimental data are compared to the
 194 data reported for fully- sp^3 bonded amorphous carbon in [20], as well as to the characteristic spectra of glassy
 195 carbon (in which the ~ 285 eV feature is labeled as *) and nanocrystalline diamond (whose characteristic post-
 196 edge structure is labeled as \S). Low-loss spectra exhibit a characteristic downshift in the plasmon-related
 197 features, both before (a) and after (b) thermal processing.

198



199 For the sake of comparison, Fig. 3c reports our experimental data together with the EELS
 200 spectrum collected from the fully sp^3 -bonded amorphous carbon phase investigated in [20]:
 201 the mutual similarity is striking, particularly considering that both spectra entirely lack the
 202 features associated with glassy carbon and nanocrystalline diamond (marked as * and § in the
 203 respective reference spectra). The EELS features in the low-energy-loss range reported in
 204 Figs. 3d and 3e exhibit plasmon peaks which are indicative of the electron densities in the
 205 corresponding phases. Both before and after thermal annealing, a systematic shift to lower
 206 energy losses of the plasmon peak positions is observed from the nanostructures with
 207 respect to the ~ 34 eV peak, which is characteristic of the surrounding diamond matrix [14,
 208 34, 35, 36]. These shifts can be interpreted on the basis of the lower atomic density of the
 209 nanostructures, by adopting the following formula [36-38]:

$$E_p = \sqrt{\frac{n_e \cdot e^2}{\epsilon_0 \cdot m^*}}$$

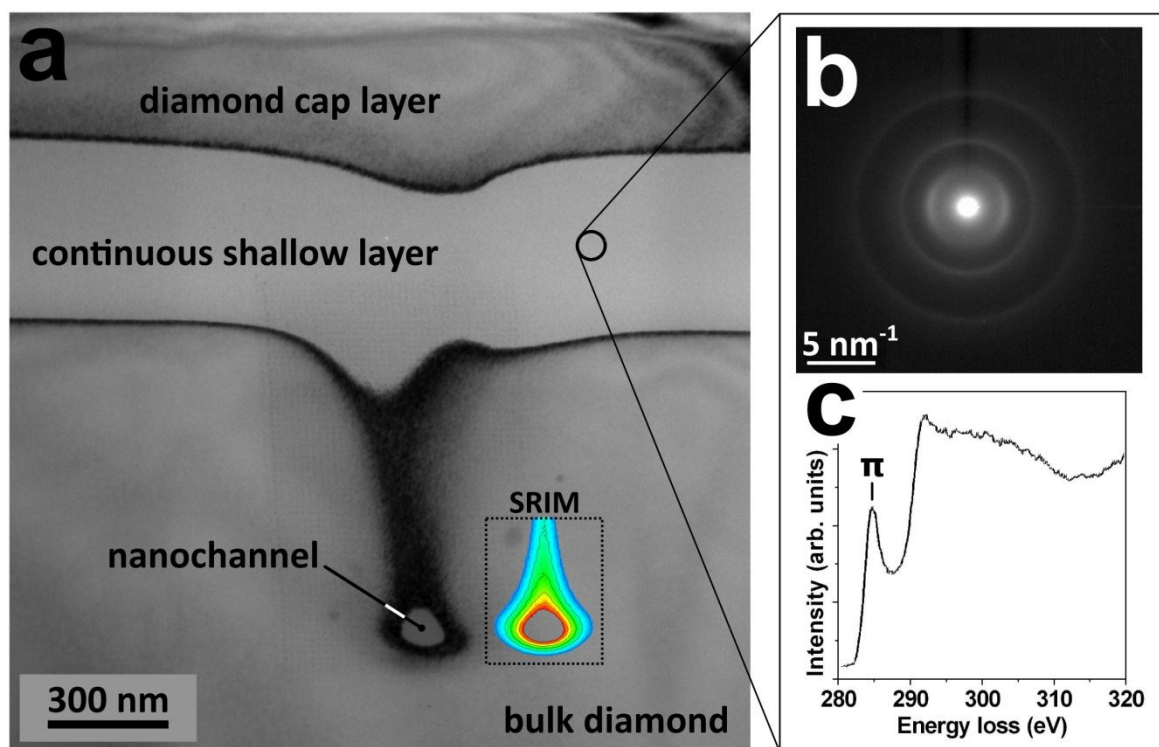
212 where E_p is the plasmon energy, m^* and e are the effective mass and charge of electron, ϵ_0 is
 213 the vacuum dielectric constant and n_e is the valence electron density.

214 Given the mass density (i.e. 3.515 g cm^{-3}) and plasmon peak position (i.e. ~ 34 eV) of the
 215 surrounding diamond matrix, and under the assumption that the same electron effective mass
 216 can be adopted for the different phases under investigation [38], it is possible to estimate the
 217 electron and (and thus mass) density within the nanochannels from the position of the
 218 corresponding plasmon peaks. Under these approximations, the (31.0 ± 0.3) eV and
 219 (32.6 ± 0.3) eV plasmon peak positions measured from the nanostructures before and after
 220 thermal annealing yield mass density estimations of $(2.92 \pm 0.06) \text{ g cm}^{-3}$ and
 221 $(3.27 \pm 0.07) \text{ g cm}^{-3}$, respectively.

222 This result is indicative of the fact that: i) the implantation process results in a substantial
 223 density variation within the nanochannels, despite the strong compressive stress exerted by
 224 the rigid surrounding diamond matrix; and ii) the disappearing of sp^2 bonds within the
 225 nanochannels upon thermal annealing determines a substantial increase of mass density with
 226 respect to the as-implanted sample, which closely approaches the density of pristine diamond
 227 and is fully compatible with the estimation (i.e. 3.3 g cm^{-3}) provided for the fully sp^3 -bonded
 228 amorphous carbon phase reported in [20].
 229



230 Finally, we remark that thermal annealing results in radically different structural features
 231 across the previously defined “continuous shallow layer” located above the nanostructures
 232 (see Fig. 4a). While (as much as observed from the nanochannels) the continuous shallow
 233 layer is characterized by TEM diffractometry features that are indicative of a fully
 234 amorphized phase (see Fig. 4b), the EELS spectrum (see Fig. 4c) exhibits the strong
 235 absorption pre-edge peak at ~ 285 eV. Such a difference is attributed to the different
 236 geometries of the two types of structures, while all other fabrication and processing
 237 parameters (irradiation, thermal annealing) are the same. This strongly indicates that the
 238 peculiar stress field developed in correspondence of the nanostructures is primarily
 239 responsible for the formation of an amorphous full- sp^3 network.
 240



241
 242 **Fig. 4** Structural properties of the continuous shallow layer located above the nanostructures, following thermal
 243 annealing. **a** Cross sectional bright-field TEM micrograph from the annealed structure: the labels indicate the
 244 diamond cap layer, the continuous shallow layer and the nanochannel embedded in the bulk diamond; the inset
 245 labeled by “SRIM” reports the two-dimensional damage density plot reported in Fig. 1c, for sake of
 246 comparison. **b** TEM diffraction pattern collected from a random region of the continuous shallow layer. **c**
 247 Corresponding EELS spectrum, clearly exhibiting the strong absorption pre-edge peak at ~ 285 eV which is
 248 indicative of a large fraction of sp^2 bonds.
 249
 250

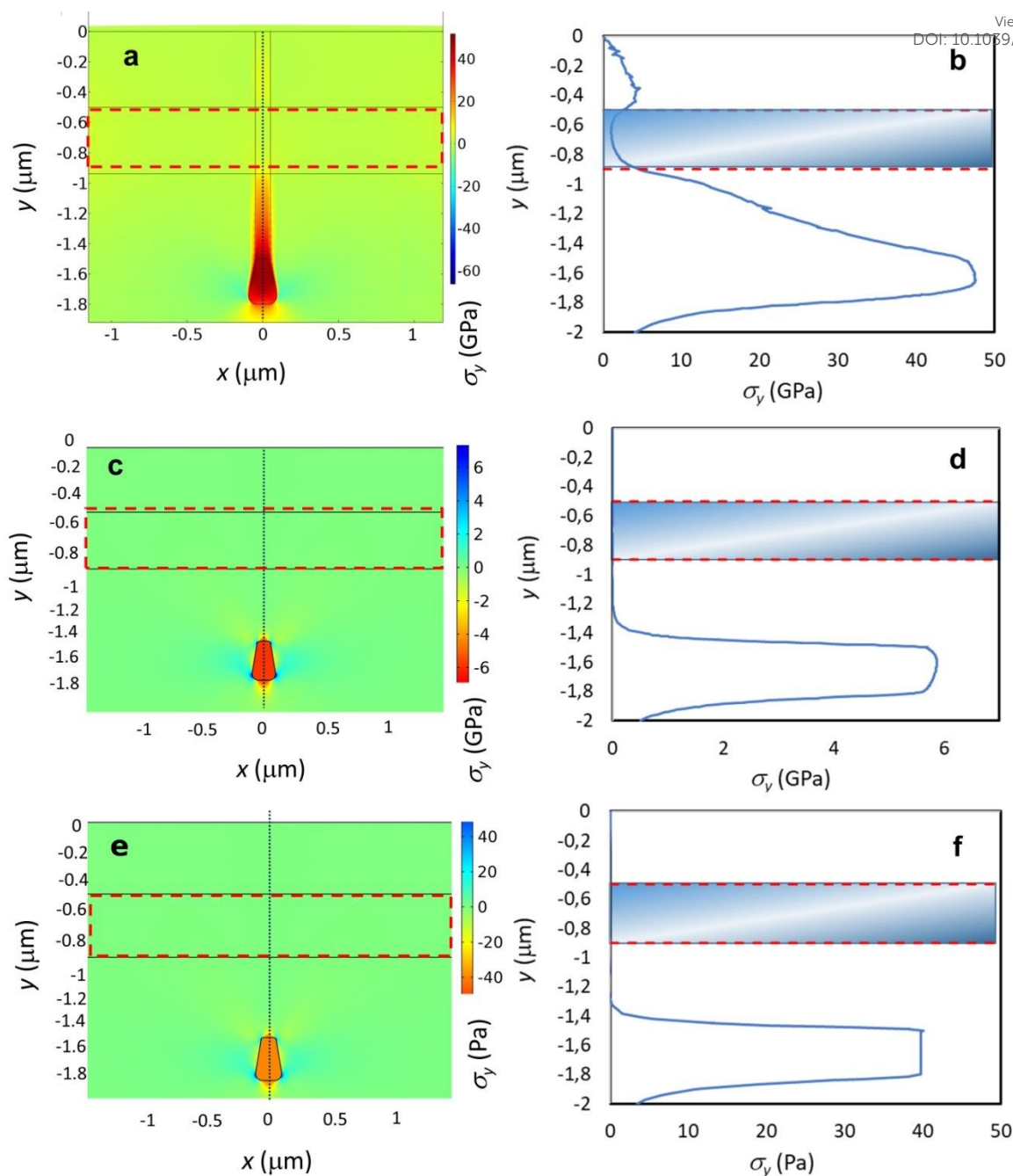


251 Our interpretation is confirmed by 2D finite element method (FEM) mechanical analysis View Article Online
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252 simulating the constrained expansion undergone by the two implanted regions, it is possible
253 to highlight a significant volumetric stress build up in the 40–50 GPa range (consistently with
254 results in [20]) upon ion implantation.

255 However, as shown in Fig. 5a, the shallow layer (region encircled by the dashed line) does
256 not undergo significant stresses in the vertical (y) direction, while the latter tends to
257 accumulate in the end-of-range region of the nanochannel, due to the confining effect of the
258 surrounding pristine diamond material. The depth variation of σ_y stresses in the nanochannel
259 (Fig. 5b), which reach a peak value of about 48 GPa, while remaining negligible in the
260 shallow layer (shaded area), are identified as the factors that are responsible for the different
261 structures observed in the two regions. Figs. 5c and 5d show the results of analogous
262 numerical simulations carried for the nanostructure after thermal annealing, under the
263 assumption that the latter process results in a conversion to a graphitic phase. In this case, a
264 distribution of relatively high compressive stresses (in the GPa range) still persists. It is worth
265 remarking that stress fields of this order of magnitude are indeed observed in graphitized
266 microstructures created with this technique, such as the ones reported in [22]. The
267 experimental observation that thermal annealing does not result in the graphitization of the
268 nanostructure is therefore attributed to the fact that the strong stress fields established around
269 the nanostructure upon ion implantation are instead fully relaxed (i.e. residual stresses in the
270 Pa range) upon the formation of a fully sp^3 -bonded amorphous carbon phase, as confirmed by
271 the simulations reported in Figs. 5e and 5f. In our interpretation, the stress state responsible
272 for the transition to sp^3 bonds is established before the thermal annealing. The initially
273 strongly stressed nanochannels therefore transition to a fully sp^3 -bonded amorphous phase
274 upon thermal annealing, and only subsequently are the stresses relaxed.

275 As mentioned above, an experimental assessment of the local stresses established across
276 amorphized/graphitized structures embedded in the diamond matrix is in general possible by
277 means of confocal micro-Raman spectroscopy, both before and after thermal annealing, as
278 already demonstrated for micrometer-sized regions [22]. This was not possible (either by
279 conventional or tip-enhanced Raman spectroscopy) in the case of the nanostructures reported
280 in the present work, due to (respectively) limited spatial resolution and spectral sensitivity of
281 the available techniques. Nonetheless, it is worth remarking that EELS provided direct
282 experimental insight into the local mass density of the nanostructures, which directly
283 translated into the above-described numerical simulations.





284

285 **Fig. 5** Results of FEM simulations of stress distributions across the structures. **a** Map of the principal stress in286 the vertical direction (σ_y) in a cross section of the as-implanted diamond: stresses develop in the nanochannel,287 and are negligible in the shallow layer (dashed line). **b** σ_y variation along the dotted line in **a**; the shaded region288 indicates the shallow layer location. **c, d** Results of analogous simulations carried for the nanostructure after

289 thermal annealing, under the assumption that this process results in a conversion to a graphitic phase: residual

290 stresses in the GPa range are still persistent. **e, f** Results of analogous simulations carried for the nanostructure

291 after thermal annealing, under the assumption that the latter process results in a conversion to a fully

292 sp^3 -bonded amorphous carbon phase: very small residual stresses in the 10 Pa range are obtained in this case.

293



294 3. Conclusions

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295 In conclusion, the reported results indicate the possibility of creating an amorphous carbon
296 phase entirely based on sp^3 chemical bonds, by means of ion-induced structural damage in
297 nanometer-sized regions embedded within the bulk diamond structure, followed by thermal
298 annealing. As confirmed by numerical simulations, the strong three-dimensional mechanical
299 stress state developed within the nanostructures is the required condition for the formation of
300 this peculiar carbon phase without the need of applying external pressure during the
301 annealing process: the key role played in the formation of this phase by internal stress fields
302 surrounding the nanostructures is demonstrated by the fact that control structures with
303 different geometries, and hence stress states, produce a radically different amorphous phase
304 containing a substantial fraction of sp^2 bonds. It is worth remarking that, although playing an
305 essential role, the high mechanical stresses established across the nanostructures are not
306 sufficient for the formation of the reported fully sp^3 -bonded amorphous phase. As reported in
307 Fig. 3a, a fraction of sp^2 -bonded carbon is indeed persistent in the strongly stressed
308 nanostructures formed upon ion implantation, and it is converted only upon the subsequent
309 thermal annealing. The necessity of carefully controlling both pressure and temperature
310 parameters for the formation of the reported carbon phase is qualitatively consistent with
311 what is reported in previous works [17-19] and particularly in Ref. [20]. Furthermore, it is
312 coherent with our current understanding of the complex pressure temperature landscape
313 around the triple point in the phase diagram of carbon [23]. We envisage that an accurate
314 numerical simulation of this carbon-based system in the reported range of
315 pressure/temperature parameters would shed significant insight into the mechanisms leading
316 to the formation of the fully sp^3 -bonded amorphous carbon phase.

317 The results presented in this work shed useful insight into the mechanisms leading to the
318 formation of fully- sp^3 -based amorphous phases in carbon, and display appealing applications
319 in fields where high-pressure carbonaceous phases could be implemented in integrated
320 devices, such as for example room-temperature superconducting devices [39].

321 Besides the fundamental relevance of this finding in the understanding of the formation of
322 exotic carbon phases, the use of focused/collimated ion beams enables the direct fabrication
323 of such nanostructures in complex patterns and arrangements, with appealing perspectives in
324 nanomechanical systems and integrated nano-optics.

325

326



327 4. Methods

328

329 4.1 Samples

330 The experiments were performed with equivalent results on different types of
331 commercially-available artificial single-crystal diamond samples, namely a $3\times 3\times 0.5\text{ mm}^3$
332 sample produced by Element SixTM with the Chemical Vapor Deposition technique, and a
333 $3\times 3\times 1.5\text{ mm}^3$ sample produced by Sumitomo ElectricTM with the High pressure High
334 Temperature synthesis technique. The former sample is classified as a type IIa “optical
335 grade” crystal, with substitutional nitrogen and boron concentrations lower than 1 ppm and
336 0.05 ppm, respectively. The latter sample is classified as a type Ib crystal, with substitutional
337 nitrogen concentration comprised between 10 ppm and 100 ppm. In both cases, the samples
338 are cut along the 100 crystal direction and are optically polished on the two opposite large
339 faces. After accurate surface cleaning, a $\sim 1.3\text{ }\mu\text{m}$ thick Cu layer was deposited by thermal
340 evaporation in high vacuum conditions. Conventional FIB micromachining with a 30 keV
341 Ga^+ ion beam was used for the mask fabrication. A Quanta 3D FEG DualBeamTM apparatus
342 equipped with Nanometer Pattern Generation System (from J. C. Nability) was used for the
343 patterning of linear nano-apertures of 100 nm width. A protective thin layer ($\sim 100\text{ nm}$) of the
344 mask was left in correspondence of each aperture, in order to avoid the superficial damage
345 induced by Ga^+ ions. After the FIB mask definition, the sample was irradiated with a beam of
346 1 MeV He^+ ions at the 0° beam line of the AN2000 accelerator of the INFN National
347 Laboratories of Legnaro. Ion current density was $\sim 500\text{ nA mm}^{-2}$ and the irradiation fluence
348 was $5\times 10^{16}\text{ cm}^{-2}$.

349 4.2 Samples characterization

351 Sample characterization was performed at the Microscopy laboratories of the Bio21 Institute
352 (University of Melbourne). 150-nm-thick cross-sectional lamellae were cut in the $\{110\}$
353 crystallographic direction by conventional FIB micromachining employing 30 keV Ga^+ ions.
354 In order to reduce FIB-induced damage layers, the lamellae were finally cut with a 5 keV Ga^+
355 beam from the same FIB facility. High-resolution transmission electron microscopy
356 (HRTEM) were performed with a Tecnai TF20 electron microscope (S-TWIN objective lens,
357 0.24 nm point resolution) transmission electron microscope operated at 200 keV. Selected
358 area diffraction patterns (SADP) were collected with smallest aperture ($\sim 180\text{ nm}$ effective
359 diameter in specimen plane). Electron energy loss spectroscopy (EELS) measurements and



360 spectrum imaging were conducted in STEM mode, with 1 nm probe beam diameter, 2.2 mrad
 361 convergence semi-angle and 16 mrad collection semi-angle at 200 kV (FEI Tecnai TF30)
 362 using Gatan GIF Quantum™ 965 energy filter with dual EELS capability. All TEM and
 363 EELS data processing was carried out using Gatan Digital Micrograph (DM) software.

364

365 4.3 Numerical simulations

366 The MeV ion induced structural damage profiles were numerically modeled by means of the
 367 SRIM Monte Carlo Code (2013.00 version) [27]. All simulations were performed in the
 368 “Detailed calculation with full damage cascades” mode, by setting a displacement energy
 369 value of 50 eV for diamond [40, 41]. The beam was assumed to be impinging on the surface
 370 at normal incidence with the mask perfectly aligned to the ion beam. A large (i.e. >100'000)
 371 number of ion trajectories was simulated. The SRIM output yields profiles of linear damage
 372 density, parameterized as number of vacancies per unit length in the depth direction.
 373 Volumetric vacancy densities were estimated from the above-said linear density profiles and
 374 the implantation fluences, by modeling the cumulative effect of implanted ions within a
 375 simple linear approximation, which does not take into account complex processes such as
 376 self-annealing, ballistic annealing and defect interaction.

377 To gain further insight in the process of amorphization and estimate the stresses acting on the
 378 irradiated region, 2-D FEM simulations were performed using Comsol Multiphysics.
 379 Consistently with the results of cross-sectional TEM microcopy (see Fig. 4a), a 5×5 μm²
 380 diamond cross section was considered, in which a 0.1×1.8 μm² implanted diamond strip is
 381 incorporated, representing the nanochannel, including a terminal trapezoidal region to
 382 account for straggling effects, and a 5×0.5 μm² strip representing the shallow layer (see
 383 Fig. 5). For the as-implanted sample, material parameters are: diamond density
 384 $\rho_d = 3.52 \text{ g cm}^{-3}$, amorphous carbon density $\rho_{ac} = 2.06 \text{ g cm}^{-3}$, diamond Young's modulus
 385 $E_d = 1220 \text{ GPa}$, amorphous carbon Young's modulus $E_{ac} = 21.38 \text{ GPa}$, [42, 43]. The density
 386 of the implanted region before annealing was calculated as a function of the induced damage
 387 density as reported in [44], i.e.:

388

$$389 \quad \rho(y) = \rho_d - (\rho_d - \rho_{ac}) \cdot \Phi(y)$$

390

$$\Phi(y) = 1 - \exp \left[- \frac{F \cdot \lambda(y)}{\gamma(1 - \rho_{ac}/\rho_d)} \right]$$



391 where $\gamma = 1.77 \times 10^{23} \text{ cm}^{-3}$ is the atomic density of diamond, F is implantation fluence and N
392 is the linear vacancy density, as derived from SRIM code. The equation accounts for defect
393 recombination and damage saturation effects occurring in the crystal [45].

394 The Young's modulus decrease as a function of the vacancy density can be expressed as:

$$395 \quad E(y) = E_d - (E_d - E_{ac}) \cdot \Phi(y)$$

396 The density decrease due to irradiation generates a constrained expansion of the implanted
397 volume, i.e. residual strains in the $i = x, y$ directions that can be expressed as follows:

$$398 \quad \varepsilon_i(y) = \sqrt[3]{\frac{\rho_d}{\rho(y)}} - 1$$

399 In the case of the sample after thermal annealing, the simulations were carried under two
400 alternative hypotheses, i.e. a conversion of the nanostructure to a graphitic phase (see Figs. 5c
401 and 5d) or to a fully sp^3 -bonded amorphous carbon phase (see Figs. 5e and 5f). In the former
402 case, the following structural parameters were adopted: $\rho_g = 2.1 \text{ g cm}^{-3}$, Young's modulus
403 $E_g = 21 \text{ GPa}$. In the latter case, the following structural parameters were adopted:
404 $\rho_{a-d} = 3.3 \text{ g cm}^{-3}$ [20, this work], $E_{a-d} = 1123 \text{ GPa}$ [20].

406 **Authors contributions**

407 F.P. conceived this study and coordinated the experimental campaign. A.B. and F. S. M.
408 prepared the samples (masking and post-irradiation processing). V. R. and F. P. prepared the
409 samples (ion irradiation). F. B. developed the numerical model of the internal stresses. P. O.
410 contributed to data analysis and compiled the manuscript (with contributions from all co-
411 authors). S. R. performed TEM and EELS characterization.

413 **Conflicts of interest**

414 There are no conflicts to declare.

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446 **References**View Article Online
DOI: 10.1039/D1NA00136A

- 447 [1] B. Sundqvist, Carbon under pressure. *Phys. Rep.* 1-73, 909.
- 448 [2] Yang, N. (guest ed.) *Novel Aspects of Diamond - From Growth to Applications* (Springer,
449 2019).
- 450 [3] Jackman, R. B. et al. (guest ed.) Special issue on diamond electronics. *Semicond. Sci.*
451 *Technol.* **18**, S1-S140 (2003).
- 452 [4] Acosta, V. et al. (guest ed.) Nitrogen-vacancy centers: Physics and applications. *MRS*
453 *Bull.* **38**, 127-167 (2014).
- 454 [5] Nemanich, R. J. et al. (guest ed.) CVD diamond - Research, applications, and challenges.
455 *MRS Bull.* **39**, 490-548 (2014).
- 456 [6] Demazeau, G. A century of high pressure: technological and scientific developments. *C.*
457 *R. Chim.* **12 (9)**, 933-942 (2009)
- 458 [7] Varnin, V. P. et al. The state of the art in the growth of diamond crystals and films. *Inorg.*
459 *Mater.* **42**, S1-S18 (2006).
- 460 [8] Hess, P. The mechanical properties of various chemical vapor deposition diamond
461 structures compared to the ideal single crystal. *J. Appl. Phys.* **111 (5)**, 051101 (2012).
- 462 [9] Li, G. et al. The manufacturing and the application of polycrystalline diamond tools - A
463 comprehensive review. *J. Manuf. Sci. Eng.* **56 (A)**, 400-416 (2020).
- 464 [10] Gruen, D. M. Nanocrystalline diamond films. *Annu. Rev. Mater. Sci.* **29**, 211-259 (1999)
- 465 [11] Huang, Q. et al. Nanotwinned diamond with unprecedented hardness and stability.
466 *Nature* **510**, 250-253 (2014).
- 467 [12] Al Mahmud, K. A. H. An updated overview of diamond-like carbon coating in tribology.
468 *Crit. Rev. Solid State* **40 (2)**, 90-118 (2015).
- 469 [13] Tyagi, A. A critical review of diamond like carbon coating for wear resistance
470 applications. *Int. J. Refract. Hard. Met.* **78**, 107-122 (2019).
- 471 [14] LiBassi, A. et al. Density, sp³ content and internal layering of DLC films by X-ray
472 reflectivity and electron energy loss spectroscopy. *Diam. Relat. Mater.* **9**, 771-776 (2000).
- 473 [15] Robertson, J. Diamond-like amorphous carbon. *Mater. Sci. Eng. R: Rep.* **37**, 129-281
474 (2002).
- 475 [16] McKenzie, D. R. et al. Compressive-stress-induced formation of thin-film tetrahedral
476 amorphous carbon. *Phys. Rev. Lett.* **67**, 773-776 (1991).
- 477 [17] Lin, Y. et al. Amorphous diamond: a high-pressure superhard carbon allotrope. *Phys.*
478 *Rev. Lett.* **107**, 175504 (2011).



- 479 [18] Goncharov, A. F. Graphite at high pressure: pseudomelting at 44 GPa. *Zh. Eksp. Teor. Fiz.* **98**, 1824–1827 (1990). New Article Online
DOI: 10.1039/D1NA00136A
- 480
- 481 [19] Yao, M. et al. Transparent, superhard amorphous carbon phase from compressing glassy
482 carbon. *Appl. Phys. Lett.* **104**, 021916 (2014).
- 483 [20] Zeng, Z. et al. Synthesis of quenchable amorphous diamond. *Nat. Comm.* **8**, 322 (2017).
- 484 [21] Praver, S. et al. Investigation of carbon near the graphite-diamond-liquid triple point.
485 *Phys. Rev. Lett.* **69** (20), 2991-2994 (1992).
- 486 [22] Olivero, P. et al. Splitting of photoluminescent emission from nitrogen–vacancy centers
487 in diamond induced by ion-damage-induced stress. *New J. Phys.* **15**, 043027 (2013).
- 488 [23] Hunn, J. D. et al. Raman Scattering from MeV-ion implanted diamond. *Phys. Rev. B* **52**
489 **(11)**, 8106 (1995).
- 490 [24] Cagliero, S. et al. Insight into non-linearly shaped superconducting whiskers via a
491 synchrotron nanoprobe. *Supercond. Sci. Technol.* **25** (12), 125002 (2021).
- 492 [25] Torsello, D. et al. Monte Carlo analysis of the oxygen knock-on effects induced by
493 synchrotron x-ray radiation in the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ delta superconductor. *Phys. Rev. Mater.* **2**
494 **(1)**, 14801 (2018).
- 495 [26] Mino, L. et al. Maskless x-ray writing of electrical devices on a superconducting oxide
496 with nanometer resolution and online process monitoring. *Sci Rep.* **7**, 9066 (2017).
- 497 [27] Ziegler, J. F. et al. *2008 SRIM—The Stopping and Range of Ions in Matter* (Morrmville,
498 NC: Ion Implantation Press)
- 499 [28] Gippius, A. A. et al. Formation and characterization of graphitized layers in ion-
500 implanted diamond. *Diamond Relat. Mater.* **8**, 1631-1634 (1999).
- 501 [29] Hickey, D. P. et al. Amorphization and graphitization of single-crystal diamond - A
502 transmission electron microscopy study. *Diamond Relat. Mater.* **18**, 1353-1359 (2009).
- 503 [30] Rubanov, S. et al. Ion implantation in diamond using 30 keV Ga^+ focused ion beam.
504 *Diamond Relat. Mater.* **20**, 1160-1164 (2011).
- 505 [31] Drumm, V. S. et al. Surface damage on diamond membranes fabricated by ion
506 implantation and lift-off. *Appl. Phys. Lett.* **98**, 231904 (2011).
- 507 [32] Motochi, I. et al. Surface Brillouin scattering on annealed ion-implanted CVD diamond.
508 *Diamond Relat. Mater.* **56**, 6-12 (2015).
- 509 [33] Muller, D. A. et al. Mapping sp^2 and sp^3 states of carbon at sub-nanometre spatial
510 resolution. *Nature* **366**, 725-727 (1993).
- 511 [34] Bursill, L. A. et al. Plasmon response and structure of nanocrystalline diamond powder.
512 *Philos. Mag. A* **76** (4), 769-781 (1997).



- 513 [35] Sato, Y. et al. High energy-resolution electron energy-loss spectroscopy analysis of
514 dielectric property and electronic structure of hexagonal diamond. *Diamond Relat. Mater.* **25**,
515 40-44 (2012). View Article Online
DOI: 10.1039/D1NA00136A
- 516 [36] Cuomo, J. J. et al. Sputter deposition of dense diamond-like carbon films at low
517 temperature. *Appl. Phys. Lett.* **58** (5), 466-468 (1991).
- 518 [37] Fallon, P. J. et al. Properties of filtered-ion-beam-deposited diamondlike carbon as a
519 function of ion energy. *Phys. Rev. B* **48** (7), 4777-4782 (1993).
- 520 [38] Ferrari, A. C. et al. Density, sp^3 fraction, and cross-sectional structure of amorphous
521 carbon films determined by x-ray reflectivity and electron energy-loss spectroscopy. *Phys.*
522 *Rev. B* **62** (16), 11089-11103 (2000).
- 523 [39] Snider, E. et al. Room-temperature superconductivity in a carbonaceous sulfur hydride.
524 *Nature* **586**, 373-377 (2020).
- 525 [40] Wu, W. et al. Molecular-dynamics study of single-atom radiation damage in diamond.
526 *Phys. Rev. B* **49** (5), 3030-3035 (1994).
- 527 [41] Saada, D. et al. Transformation of diamond (sp^3) to graphite (sp^2) bonds by ion impact.
528 *Int. J. Mod. Phys. C* **9** (1), 61-69 (1998).
- 529 [42] Wei, Y. X. et al. Soft phonons and phase transition in amorphous carbon. *Phys. Rev. B*
530 **72**, 012203 (2005)
- 531 [43] Fairchild, B. A. et al. Mechanism for the Amorphisation of Diamond. *Adv. Mater.* **24**,
532 2024-2029 (2012).
- 533 [44] Battiato, A. et al. Softening the ultra-stiff: Controlled variation of Young's modulus in
534 single-crystal diamond by ion implantation. *Acta Mater.* **116**, 95-103 (2016).
- 535 [45] Bosia, F. et al. Direct measurement and modelling of internal strains in ion-implanted
536 diamond. *J. Phys. Condens. Matter* **25** (38), 385403 (2013).

