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Effects of high-power laser irradiation on sub-superficial graphitic layers in single-crystal diamond

F. Picollo^{1,2,3*}, S. Rubanov⁴, C. Tomba^{5,6,7}, A. Battiato^{2,1,3}, E. Enrico⁸, A. Perrat-Mabilon^{9,10},
C. Peaucelle^{9,10}, T. N. Tran Thi^{5,9,11}, L. Boarino⁸, E. Gheeraert^{5,7}, P. Olivero^{2,1,3,8}

¹ National Institute of Nuclear Physics (INFN), section of Torino, Italy

² Physics Department and "NIS" Inter-departmental centre, University of Torino, Torino, Italy

³ National Interuniversity Consortium for the Physical Sciences of Matter (CNISM), Torino Unit, Italy

⁴ Bio21 Institute, University of Melbourne, Australia

⁵ University of Grenoble Alpes, F-38000 Grenoble, France

⁶ Laboratoire des Technologies de la Microelectronique, Minatec Campus, F-38054 Grenoble, France

⁷ CNRS, Institute NEEL, F-38042 Grenoble, France

⁸ National Institute of Metrologic Research (INRiM), Torino, Italy

⁹ University of Lyon 1, CNRS, Inst Phys Nucl Lyon, F-69622 Villeurbanne, France

¹⁰ IN2P3, F-69622 Villeurbanne, France

¹¹ European Synchrotron Radiation Facility (ESRF), Grenoble, France

Abstract

We report on the structural modifications induced by a $\lambda = 532$ nm ns-pulsed high-power laser on sub-superficial graphitic layers in single-crystal diamond realized by means of MeV ion implantation. A systematic characterization of the structures obtained under different laser irradiation conditions (power density, number of pulses) and subsequent thermal annealing was performed by different electron microscopy techniques. The main feature observed after laser

26 irradiation is the thickening of the pre-existing graphitic layer. Cross-sectional SEM imaging was
27 performed to directly measure the thickness of the modified layers, and subsequent selective
28 etching of the buried layers was employed to both assess their graphitic nature and enhance the
29 SEM imaging contrast. In particular, it was found that for optimal irradiation parameters the laser
30 processing induces a six-fold increase the thickness of sub-superficial graphitic layers without
31 inducing mechanical failures in the surrounding crystal. TEM microscopy and EELS
32 spectroscopy allowed a detailed analysis of the internal structure of the laser-irradiated layers,
33 highlighting the presence of different nano-graphitic and amorphous layers. The obtained results
34 demonstrate the effectiveness and versatility of high-power laser irradiation for an accurate
35 tuning of the geometrical and structural features of graphitic structures embedded in
36 single-crystal diamond, and open new opportunities in diamond fabrication.

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40 * corresponding author: picollo@to.infn.it

41 ph: +39 011 670 7879

42 fax: +39 011 670 7020

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49

50 **1. Introduction**

51 Diamond is well known for its range of extreme mechanical, thermal and optical properties,
52 which make it an attractive material for a variety of applications [1]. Nevertheless, diamond is a
53 metastable allotropic form of carbon at standard pressure and temperature, and can be converted
54 into graphite if an energy barrier is overcome [2]. Several approaches have been developed to
55 induce this phase transition, among which ion-beam-induced graphitization [3–9] and laser-
56 induced graphitization [10,11] play a prominent role. The former approach takes advantage of
57 the ion-induced defect creation caused by nuclear collisions to amorphize the material and the
58 subsequent thermal annealing to convert amorphized regions into a graphitic phase [3]. The latter
59 approach is based on complex non-equilibrium dynamics induced by high-power light
60 absorption, which were modelled with different theoretical approaches based on the non-
61 radiative recombination of electron-hole pairs [11] or on a non-thermal ultrafast non-equilibrium
62 phase transition [12,13].

63 Several previous studies explored the laser-induced graphitization process of single-crystal
64 diamond: the first investigations dating back to the 80's were focused on realization of graphitic
65 structures on diamond surface with direct writing or optical projection by means of excimer
66 lasers [14], approached that was further investigated also in recent years [15]. Subsequently, new
67 theoretical models of pulsed laser irradiation were proposed taking into account fast energy
68 transfer mechanisms [16]. Consequently, in the last decade several works were carried out to
69 exploit the possibility of realizing three-dimensional structures into diamond bulk by means of
70 femtosecond [17,18] and picosecond [18–20] pulsed laser writing. Furthermore, the possibility of
71 enhancing the resolution in the laser fabrication of the graphitic structures with the use of
72 adaptive optical elements was recently demonstrated [21,22].

73 Direct laser-induced graphitization represents an extremely versatile technique with promising
74 applications in different fields such as the realization of diamond-based particle detectors [23–
75 27] and (upon the selective removal of the graphite) microfluidics devices for biomedical sensing
76 [28].

77 On the other hand, this technique is limited by the poor geometrical quality of structures
78 finishing, which is inherently caused by the nature of the graphitization process [18,20]. In order
79 to overcome this limitation, laser-induced graphitization in diamond can be combined with a
80 preliminary MeV-ion-induced graphitization stage. By taking advantage of the high degree of
81 control on the geometrical properties (depth, thickness) of MeV-ion-induced buried graphitic
82 structures in diamond allowed by the peculiar nuclear energy loss profile of MeV ions [29], this
83 double-step procedure guarantees a better definition in the material micro-structuring [30] and
84 also represents an interesting improvement in the realization of particle detectors [26,31,32],
85 bolometers [33,34], bio-sensors [35–37], metallic-dielectric structures [38] and microfluidics
86 [39].

87 In the present paper we report on the use of ns-pulsed laser irradiation for the structural
88 modification and thickening of sub-superficial graphitic layers in diamond, which were realized
89 by means of MeV ion implantation. The above-mentioned structures are imaged before and after
90 the selective removal of the graphitic phase with respect to the surrounding diamond matrix, and
91 are characterized in their structural properties by transmission electron microscopy.

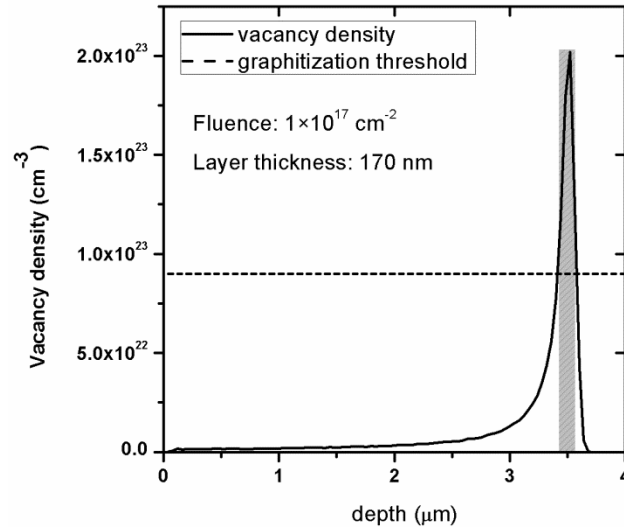
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93 **2. Experimental**

94 In the present study, a commercial synthetic (001) single-crystal diamond grown by High
95 Pressure High Temperature method (HPHT) by ElementSix (Ascot, UK) was used. The diamond

96 is $3 \times 3 \times 0.3 \text{ mm}^3$ in size and it is classified as type Ib, having a nominal substitutional nitrogen
97 concentration between 10 ppm and 100 ppm. The sample is cut along the 100 crystal direction
98 and it is optically polished on the two opposite large faces.

99 The sample was implanted at room temperature at the "Service Faisceaux d'Ions" laboratory of
100 the Nuclear Physics Institute (University of Claude Bernard Lyon 1) across one of the two main
101 polished surfaces with a broad 2 MeV He^+ ion beam to deliver a uniform fluence of $1 \times 10^{17} \text{ cm}^{-2}$
102 across the irradiated area. During the implantation, the beam current was $\sim 200 \text{ Na}$. The process
103 of damage induced by MeV ions in matter occurs mainly at the end of ion range, where the cross
104 section for nuclear collisions is strongly enhanced, after the ion energy is progressively reduced
105 by electronic interactions occurring in the initial stages of the ion path [40]. Figure 1 shows the
106 strongly non-uniform depth profile of the density of induced vacancies ($\#_{\text{vac}} \text{ cm}^{-3}$) evaluated in a
107 linear approximation as the product between the implantation fluence ($\#_{\text{ions}} \text{ cm}^{-2}$) and the linear
108 density of induced vacancies per single ion ($\#_{\text{vac}} \text{ cm}^{-1} \#_{\text{ions}}^{-1}$). The latter quantity was estimated
109 with the "Stopping and Range of Ions in Matter" (SRIM)-2013.00 Monte Carlo code [29] in
110 "Detailed calculation with full damage cascade" mode by taking an atom displacement energy
111 value of 50 eV [41]. The high density of damage induced by ion implantation promotes the
112 conversion of the diamond lattice to an amorphous phase, which is located $\sim 3.5 \mu\text{m}$ below the
113 sample surface.



114

115 Fig. 1: Depth profile of the volumetric vacancy density induced in diamond by 2 MeV He⁺ implanted at a fluence of
 116 $1 \times 10^{17} \text{ cm}^{-2}$. The graphitization threshold is reported in dashed line. The amorphized region is highlighted by the
 117 grey area in correspondence of the intersection of the Bragg peak with the graphitization threshold.

118

119 The above-mentioned implantation fluence allowed to overcome a critical damage density,
 120 usually referred as “graphitization threshold” [42], whose value in the above-mentioned linear
 121 approximation has been estimated as $\sim 9 \times 10^{22} \text{ cm}^{-3}$ for light MeV irradiation [43], as indicated in
 122 Figure 1. Such a model of the damage profile has to be considered as a rough estimation since it
 123 results from a linearly cumulative effect of ion damage, i.e. by neglecting any damage saturation
 124 effects occurring at high damage levels such as self-annealing and vacancies interactions [44,45].
 125 Nonetheless, in this context it can be considered as a satisfactory approach to estimate the depth
 126 and thickness of the buried region. After ion implantation, the sample was thermally annealed for
 127 1 hour at a temperature of 900 °C, which is suitable for the conversion of amorphous carbon to a
 128 graphitic phase, as confirmed by TEM studies [46–48]. Concurrently, the annealing process
 129 restores the pristine diamond structure in the lightly-damaged cap layer, i.e. the region comprised

130 between the surface and the buried graphitic layer [49,50]. The process was carried out in
131 vacuum ($p \approx 10^{-6}$ mbar) to avoid accidental etching of the diamond surface due to oxidation.

132 The ion-implanted side of the sample was subsequently irradiated with nanosecond-pulsed
133 Nd:YAG laser (EzLaze3 by New Wave) equipped with a Q-switching system. This laser source
134 generates pulses of 4 ns duration with a repetition rate of either 1 Hz or 5 Hz. Two different
135 emission wavelengths can be selected, i.e. 1064 nm and 532 nm, the second one being obtained
136 by means of an angle-tuned KTP crystal. The laser beam is focused onto the sample with a
137 microscope supplied with 5×, 20× and 100× objective lenses. The co-axial imaging through the
138 microscope offers the opportunity of monitoring the sample processing in real time. Using the
139 532 nm wavelength and the 100× objective, the maximum emission power is 150 Kw and the
140 minimum size of the spot is $5 \times 5 \mu\text{m}^2$, thus resulting in a maximum power density of
141 $\sim 22 \text{ GW cm}^{-2}$.

142 A Quanta 3D™ dual-beam system by FEI available at the "NanoFacility Piemonte" laboratories
143 of the INRiM Institute was employed to cross-section the sample by 30 keV Ga^+
144 focused-ion-beam (FIB) milling and to estimate the thickness of the graphitic layer before and
145 after the laser irradiation by SEM imaging .

146 The selective electrochemical etching of the graphite was performed with the purpose of
147 enhancing the topographical contrast in the SEM imaging of the buried layers. This process was
148 performed by immersing the sample in a water solution of H_3BO_3 ($4 \times 10^{-3} \text{ mol l}^{-1}$ concentration)
149 for 1 hour applying a DC voltage of 150–200 V through a couple of platinum electrodes placed
150 in close proximity of the sample [51].

151 The TEM imaging was performed at the Microscopy laboratories of the Bio21 Institute
152 (University of Melbourne) for a detailed study of the thickness and the structure of the graphitic

153 layers before and after laser annealing. To this scope, a Tecnai TF20 electron microscope
154 operated at 200 keV was employed. Cross-sectional TEM samples with thickness ~100 nm were
155 prepared in [110] and [100] orientations using a standard FIB lift-off technique. Selected area
156 diffraction (SAD) patterns were collected with smallest aperture (diameter ~180 nm in the
157 specimen plane). Nano-beam diffraction patterns were collected in nano-beam scanning TEM
158 (STEM) mode with beam size ~10 nm. Electron energy loss spectroscopy (EELS) was conducted
159 by employing a Gatan Enfina energy filter.

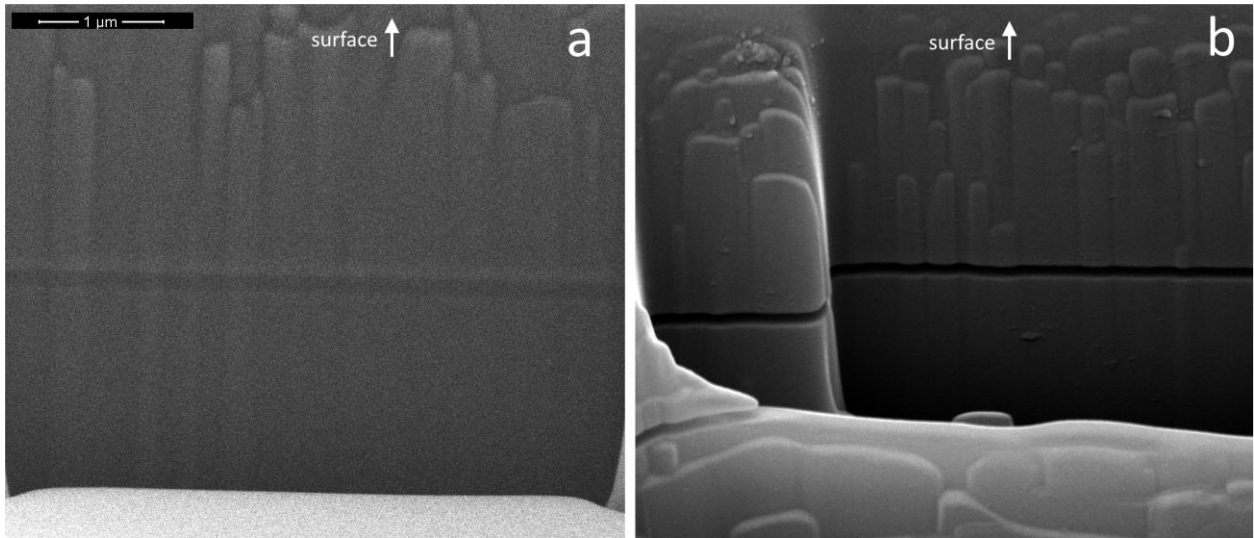
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161 **3. Results and discussion**

162 FIB milling was employed to allow the cross-sectional SEM imaging of the ion-implanted and
163 subsequently annealed regions, as shown in Fig. 2a. The presence of the graphitic layer
164 embedded in the diamond matrix can be recognized in the dark grey horizontal strip, although
165 the low contrast in the secondary emission yield between graphite and diamond does not allow
166 performing an accurate measure of its thickness.

167 Selective etching of the graphite was therefore performed in order to improve imaging contrast
168 and facilitate the measurement of the thickness of the sub-superficial layer. Fig. 2b shows a SEM
169 micrograph of the same region of the sample reported in Fig. 2a, after selective chemical etching
170 of the graphite layer. The previously graphitized region now corresponds to a gap within the
171 material, thus allowing a better visibility of its thickness and depth.

172



173

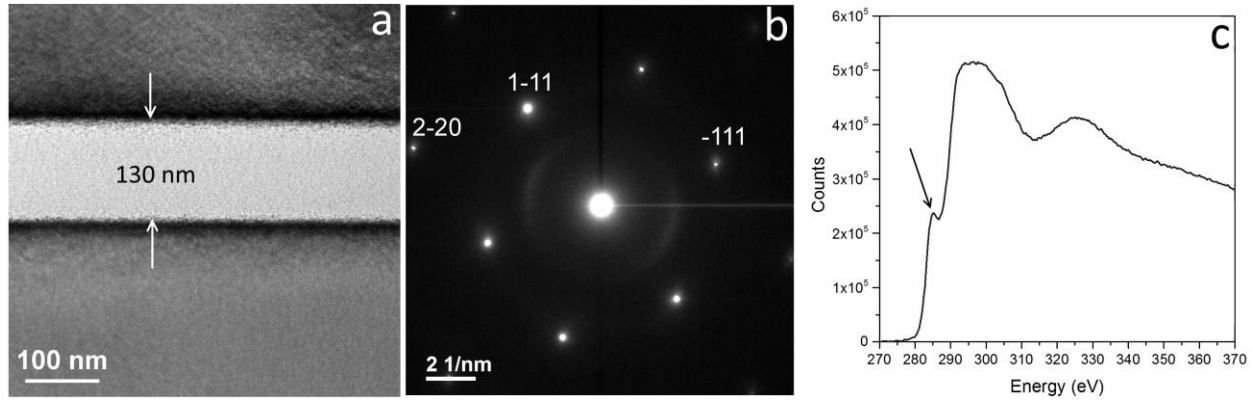
174 Fig. 2: Cross-sectional SEM micrographs of the sub-superficial graphitic layer in ion-implanted and annealed
175 diamond a) before and b) after the selective etching process. A better definition of the geometrical parameters of the
176 buried structure is clearly obtained after its selective removal by means of the etching process.

177

178 The thickness of the buried layer evaluated from Fig. 2a is (200 ± 40) nm, while it was estimated
179 (140 ± 20) nm from Fig. 2b. This discrepancy is due to the relaxation of the upper cap layer, as it
180 will be more extensively discussed in the following.

181 A more detailed structural characterization of the investigated regions was performed by means
182 of cross-sectional TEM microscopy and EELS spectroscopy. A bright-field TEM micrograph
183 and the corresponding Selected Area Diffraction (SAD) pattern of the implanted layer after
184 thermal annealing are shown in Figs. 3a and 3b, respectively. The implanted layer is clearly
185 visible due to the higher contrast and its width was estimated as (130 ± 3) nm. As shown in
186 Fig. 3b, the diffraction pattern is characterized by well-defined spots arising from the diffraction
187 of the bulk diamond, as well as arcs along the $\{220\}$ reflections from the graphitic C-planes of
188 the implanted layer. As shown in Fig. 3c, the corresponding EELS spectrum from the buried
189 graphitic layer of the same region has a prominent feature at ~ 285 eV, which is characteristic of

190 sp^2 bonding. Therefore, TEM diffraction pattern combined with EELS confirm the conversion of
 191 the implanted layer into a nanocrystalline graphitic phase with predominant orientation of
 192 C-planes normal to the diamond surface.

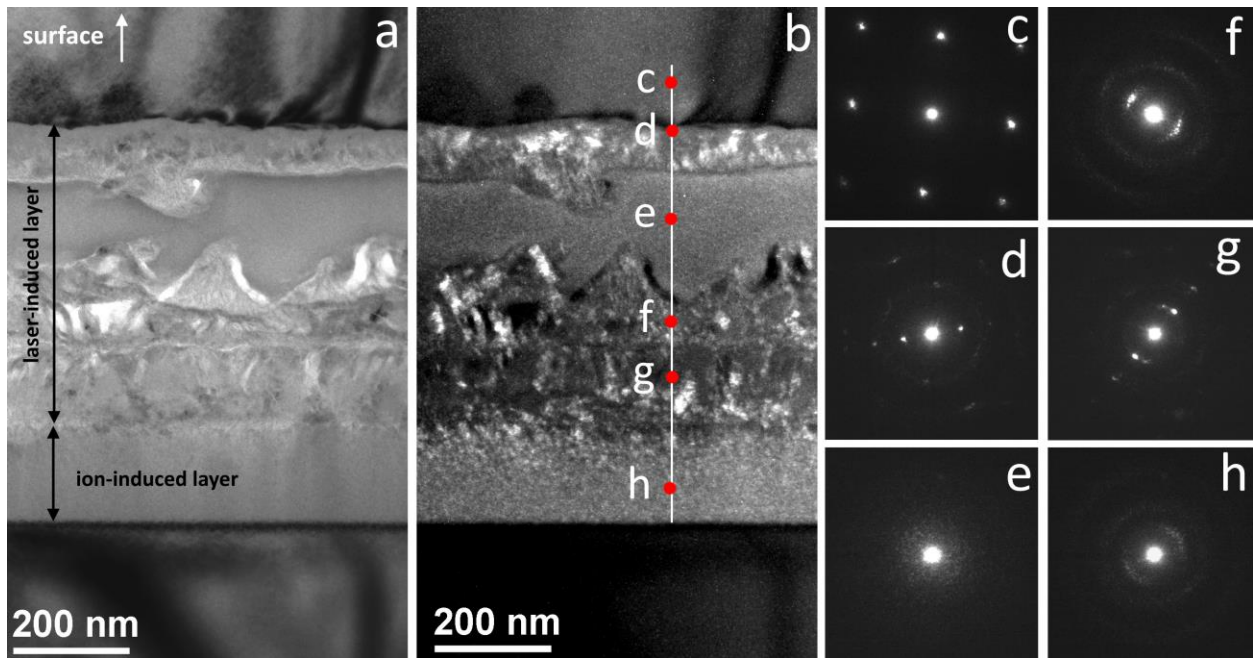


193
 194 Fig. 3: a) Bright-field TEM cross-section micrograph of the sub-superficial graphitic layer in diamond before laser
 195 irradiation (the sample surface is located towards the top of the picture). The thickness of the ion-implanted and
 196 subsequently annealed structure is highlighted, corresponding to (130 ± 3) nm. B) SAD pattern taken from the same
 197 area, showing well defined spots and arcs respectively from the diamond and graphitic regions. C) EELS spectrum
 198 of the carbon K-edge taken from the implanted layer; the characteristic feature at 285 eV is indicated by the arrow.

199
 200 Multiple-pulse laser irradiation at $\lambda = 532$ nm wavelength of the ion-implanted and subsequently
 201 annealed diamond sample was carried out at two different powers densities (namely,
 202 0.41 GW cm^{-2} and 0.45 GW cm^{-2}) over an area of $26 \times 26 \mu\text{m}^2$.

203 Cross-sectional bright- and dark-field TEM micrographs of an area irradiated with 50 laser
 204 pulses at a power density of 0.41 GW cm^{-2} are reported in Figs. 4a and 4b, respectively, and
 205 show a complex multi-layer structure within the buried layer. The laser-induced graphitic layer,
 206 formed in the region located directly above the ion-implanted layer, results in an overall
 207 thickness of (690 ± 15) nm. At the bottom of Fig. 4b (i.e. towards the bulk of the sample), the
 208 nanocrystalline graphite layer due to ion implantation is clearly distinguishable, exhibiting the

209 same thickness measured before the laser irradiation (see Fig. 2) and no appreciable differences
210 in its structure.



211
212 Fig. 4: a) Bright- and b) dark-field TEM cross section micrographs of a laser irradiated ($\lambda = 532$ nm, power density:
213 0.41 GW cm^{-2} , 50 pulses) nanocrystalline graphitic sub-superficial layer obtained after annealing at $900 \text{ }^\circ\text{C}$ of an
214 implanted diamond region. The layer thickens towards the sample surface (i.e. towards the top of the figure), with a
215 complex structuring of the modified region consisting in amorphous-carbon and nanocrystalline-graphite layers. The
216 numbered red dots in b) highlight the regions from which the diffraction patterns reported in c-h) were acquired.

217
218 The laser-induced phase transition is driven by thermal effects that originate as a consequence of
219 the strong absorption of the laser radiation by the implanted graphitic layer. Since the laser beam
220 irradiates the side of the nanocrystalline graphitic layer facing the sample surface, the induced
221 heating of the material is mainly localized within the "cap layer" comprised between the layer
222 itself and the sample surface rather than towards the bulk, and therefore graphitization mainly
223 occurs in such direction. An estimate of the temperature rise in the cap layer can be obtained
224 from the pressure-temperature phase diagram of elemental carbon [52], with a similar approach

225 to what is reported in [2]. Finite element simulation studies from diamond samples implanted
226 under the same experimental conditions [53] indicate that the regions surrounding the buried
227 graphitic layer experience pressures of 8–10 GPa due to its constrained volume expansion.
228 Furthermore, the experimental evidence indicates that the temperature rise is high enough to
229 drive the graphitization process within the corresponding stable portion of the phase diagram,
230 without incurring in its liquefaction. The laser-induced local temperature rise is therefore
231 estimated between 2500 °C and 4500 °C. Such a significant heating is expected to rapidly
232 dissipate due to the high thermal conductivity of diamond.

233 Nano-beam diffraction patterns were taken in scanning TEM mode along the line shown in
234 Fig. 4b, which is crossing perpendicularly the graphitic layer at 10 nm steps. A selection of the
235 obtained diffraction patterns are shown in Figs. 4c-h. The peculiar structure of the laser-induced
236 layer is characterized by the presence of an amorphous carbon phase (diffraction pattern in
237 Fig. 4e) comprised between two polycrystalline graphitic phases (diffraction patterns in Figs. 4d
238 and 4f), as clearly visible in the dark-field micrograph of Fig. 4b. The dark field micrograph was
239 constructed by selecting the graphitic arcs in the diffraction pattern, and therefore the graphitic
240 crystals appear as bright spots in it. These spots have <5 nm sizes in implanted layer and much
241 larger dimensions in the laser-induced layer. The observed multi-layer structure is somewhat
242 surprising and can be qualitatively attributed to a complex combination of thermal gradient and
243 stress effects occurring in the diamond during the pulsed laser irradiation [54].

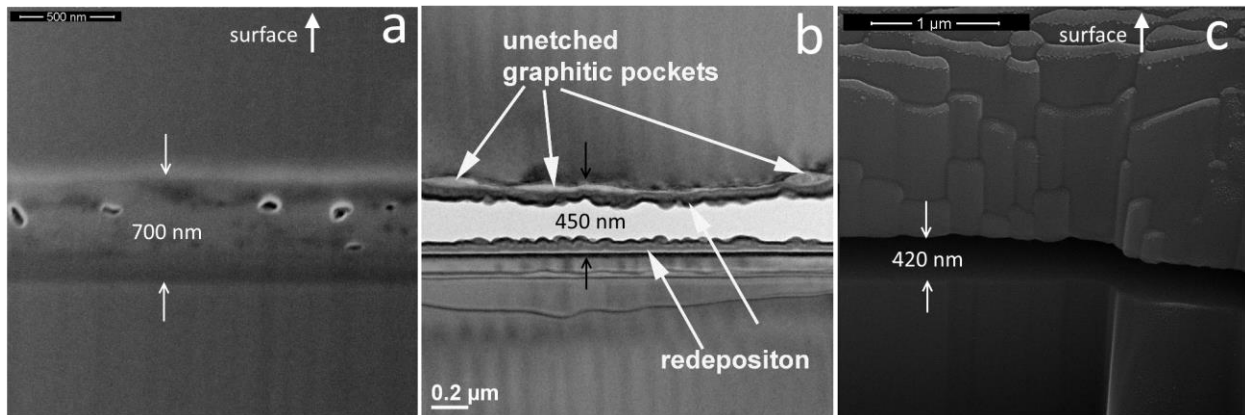
244 A SEM micrograph of the same laser-irradiated region is reported in Fig. 5a, from which a layer
245 thickness of (700 ± 70) nm can be estimated, compatibly (although with lower accuracy) with
246 what obtained from TEM imaging. The amorphous areas are visible inside the graphitic layer, as

247 well as some voids. These voids were probably filled with re-deposited material during TEM
248 sample preparation and are therefore not visible in TEM images reported in Figs. 4a and 4b.

249 Following the same procedure adopted for the sample after implantation and annealing (see
250 Fig. 2), a selective electrochemical etching was carried out and the resulting structure is shown in
251 the TEM micrograph reported in Fig. 5b. The removal of the graphitic layer is evident in both
252 micrographs. Also, re-deposited material is visible on both surfaces of the gap, as commonly
253 observed in FIB milling. As shown in Fig. 5b, after laser irradiation and chemical etching the
254 buried layer was not entirely removed, but rather only the ion-induced nanocrystalline graphite
255 layer was etched, as confirmed by the comparison of the thicknesses of the regions reported in
256 Figs. 4a and 5b. This is a surprising result, since the polycrystalline graphitic phase formed
257 during laser irradiation is expected to be effectively etched by the electrochemical attack.

258 A thermal treatment at 900 °C for 2 hours was therefore performed on the same sample after
259 laser irradiation, with the purpose of inducing the graphitization of residual amorphous/distorted
260 material in the un-etched region. Afterwards, the sample was exposed to the same etching
261 process. As shown in Fig. 5c, the width of the etched layer in the laser-irradiated and annealed
262 sample increased up to (420 ± 20) nm, indicating a full removal of the laser-irradiated layer. As
263 already reported for the sample before laser irradiation, a discrepancy between the thickness
264 values of the laser-induced layer and the remaining gap is observed (see Figs. 5a and 5c). As
265 mentioned before, this effect can be explained by considering that a relaxation of the diamond
266 cap layer takes place after the removal of the graphitic layer. Since the graphite is characterized
267 by a significantly lower atomic density with respect to diamond, a volume expansion takes place
268 upon the graphitization process [55,56], thus deforming the upper diamond cap layer comprised

269 between the graphitic layer and the sample surface. Once the graphite is removed, the cap layer
 270 undergoes a structural relaxation which induces the thinning of the etched region.

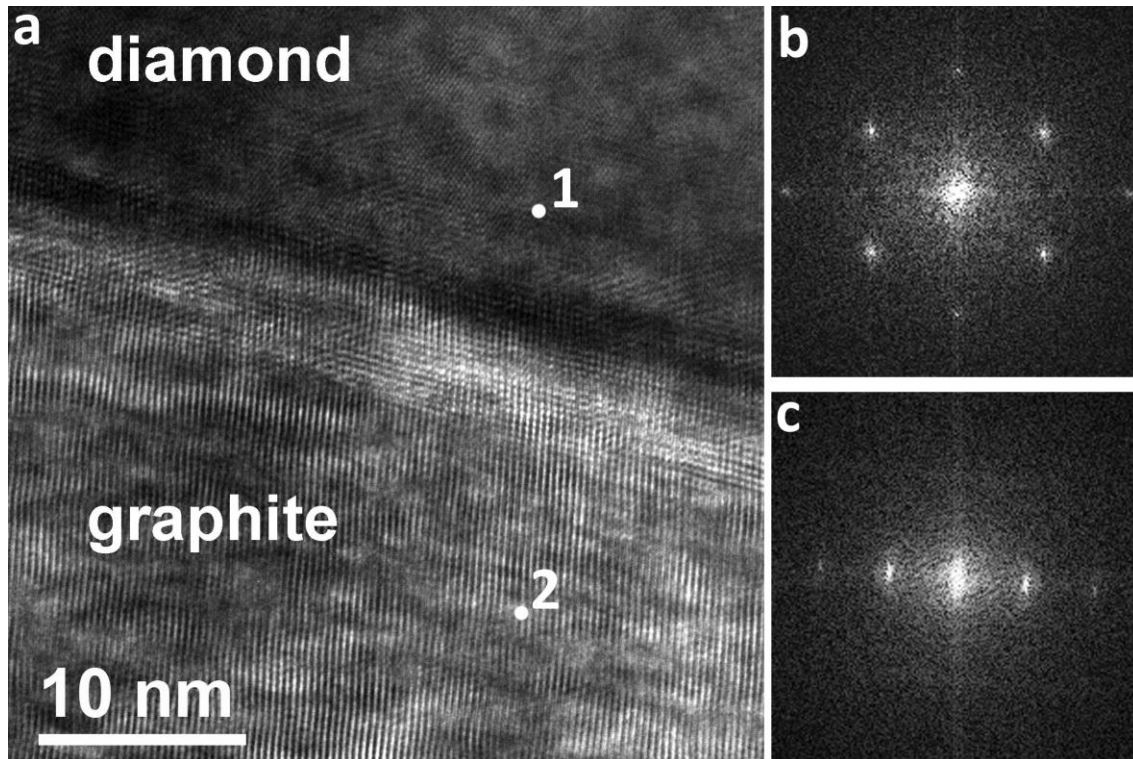


271
 272 Fig. 5: a) Cross sectional SEM micrograph of the buried damaged layer after laser irradiation ($\lambda = 532$ nm, power
 273 density: 0.41 GW cm^{-2} , 50 pulses). b) Cross-sectional TEM micrograph of the same layer reported in a) after
 274 electrochemical etching; together with the characteristic re-deposited material present in the gap, un-etched
 275 laser-induced layers are recognizable around the gap. c) Cross-sectional SEM micrograph of the same layer reported
 276 in a) after a further 900°C annealing step and electrochemical etching; no un-etched layers are visible.

277
 278 Even more surprisingly, after the first etching process (i.e. before the second annealing step)
 279 highly oriented graphitic clusters were found in correspondence of the partially un-etched
 280 diamond/graphite interface which was closest to the sample surface, as shown in Fig. 5b.

281 Fig. 6a reports a high-resolution TEM micrograph of one of these clusters. The presence of
 282 graphite C-planes is clearly visible in the corresponding diffraction pattern reported in Fig. 6c,
 283 indicating the highly oriented structure of these graphitic clusters.

284



285

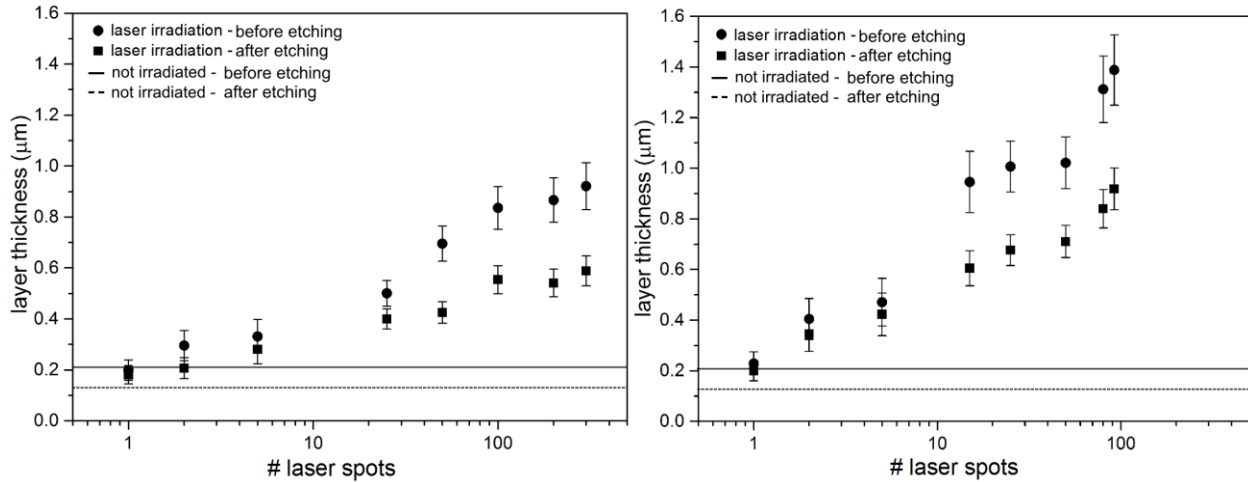
286 Fig. 6. a) High resolution TEM micrograph of one of the highly oriented graphitic clusters remaining near the
287 diamond interface after the chemical etching of the laser-irradiated sample. The corresponding diffraction patterns
288 from diamond (spot "1") and graphite (spot "2") are reported in b) and c), respectively.

289

290 The results reported so far refer to regions of the sample which were exposed to 50 laser pulses
291 and subsequently subjected to different annealing and/or etching processes. A systematic
292 investigation of the laser-induced graphitization was also carried out as a function of the laser
293 irradiation parameters (power, number of pulses). As previously reported, the implanted and
294 subsequently annealed sample was irradiated with 532 nm laser pulses and power densities of
295 0.41 GW cm^{-2} and 0.45 GW cm^{-2} over different $26 \times 26 \mu\text{m}^2$ areas. Following these laser
296 irradiations, the sample was annealed at $900 \text{ }^\circ\text{C}$ for 2 hours with the purpose of inducing a full
297 graphitization in the irradiated areas, consistently with the above-mentioned results. Also in this
298 case, cross-sectional SEM imaging of the irradiated regions was systematically performed to

299 evaluate the thickening in regions processed with different laser irradiation conditions, and the
300 layer thicknesses were measured before and after the etching process.

301 Fig. 7 summarizes the results obtained for the two different power densities for a number of laser
302 pulses ranging between 1 and 300. It is evident that the thickness of the graphitic sub-superficial
303 layer obtained after laser irradiation and thermal annealing increases at increasing numbers of
304 laser pulses, up to more than 6 times its initial value. The trends reported in Fig. 7 clearly
305 indicate a strong sub-linear dependence of the layer thickness from the number of laser pulses. It
306 is also evident that the power density has a direct influence on the thickening process, with the
307 larger power density determining a more pronounced thickening for the same number of laser
308 pulses. A maximum total thickness of $\sim 1.25 \mu\text{m}$ was achieved, with the process being limited by
309 the large mechanical stresses that build up in the diamond cap layer which ultimately cause local
310 mechanical fractures. For this reason, power densities and number of pulses larger than the ones
311 shown in Fig. 7 could not be tested without incurring in structural damage effects. Consistently
312 with what was previously observed, for all of the structures the second annealing step resulted in
313 a complete removal of the buried graphitic layers upon electrochemical etching. It is also worth
314 stressing that, as explained above, the thickness of the gaps obtained after selective
315 electrochemical etching is systematically smaller than the thickness of the laser-induced
316 graphitic layers, as shown in Fig 7.



317

318 Fig. 7: Plot of the measured thickness of the sub-superficial graphitic layers versus the number of $\lambda = 532$ nm laser
 319 pulses for two different power densities, i.e. a) $P = 0.41$ GW cm⁻² and b) $P = 0.45$ GW cm⁻². The thickness
 320 measurements are reported both before (circular dots) and after (square dots) the selective etching process. Likewise,
 321 the horizontal lines indicate the thicknesses of the pristine ion-induced layer, both before (continuous line) and after
 322 (dashed line) the selective etching process.

323

324 4. Conclusions

325 We reported on the effect of ns-pulsed $\lambda = 532$ nm laser irradiation on the thickening of
 326 sub-superficial graphitic layers in diamond obtained by means of 2 MeV He⁺ ion implantation
 327 and subsequent high-temperature annealing. Cross-sectional TEM and EELS measurements
 328 elucidated the complex structuring of the processed regions into amorphous and nanocrystalline
 329 graphitic multi-layers. The complete conversion of the laser-induced layers to an etchable
 330 graphitic phase was obtained only upon thermal annealing at 900 °C, while a highly-oriented
 331 phase was found in the residual graphitic pockets after selective etching of the non-annealed
 332 samples. A systematic SEM investigation of the thickening of the graphitic region was carried
 333 out as a function of the laser irradiation parameters (power density, number of pulses). An

334 increase up to 650% of the initial layer thickness was reached without incurring into critical
335 mechanical failures due to induced mechanical stresses.

336 By allowing a fine tuning of geometrical and structural properties of graphitic layers formed by
337 ion irradiation, laser-induced graphitization offers interesting opportunities for a new level of
338 control in the fabrication of buried graphitic structures in diamond, with appealing applications
339 in different fields in which MeV ion beam lithography and laser graphitization were successfully
340 employed [26,31–36,38,39]

341

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350

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