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*Original*

Effects of high-power laser irradiation on sub-superficial graphitic layers in single-crystal diamond / Picollo, F.; Rubanov, S.; Tomba, C.; Battiato, A.; Enrico, Emanuele; Perrat Mabilon, A.; Peaucelle, C.; T. N. Tran Thi, C.; T. N., Tran Thi; Boarino, Luca; Gheeraert, E.; Olivero, P.. - In: ACTA MATERIALIA. - ISSN 1359-6454. - 103:(2016), pp. 665-671. [10.1016/j.actamat.2015.10.046]

*Availability:*

This version is available at: 11696/54557 since: 2017-02-24T14:53:58Z

*Publisher:*

Elsevier

*Published*

DOI:10.1016/j.actamat.2015.10.046

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

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**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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44 Keywords:                      diamond, high power laser, graphitisation, TEM microscopy

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46 PACS codes:                    diamond, 81.05.ug

47                                      application of laser, 42.62.-b

48                                      graphite, 81.05.uf

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.

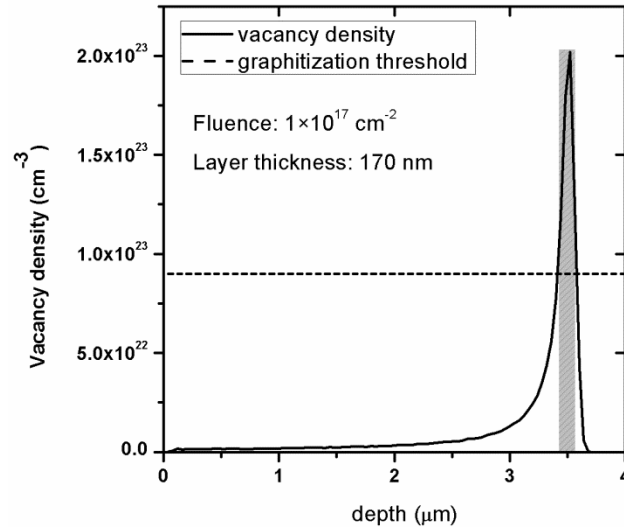
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## 93 **2. Experimental**

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  $\text{He}^+$  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  $\text{He}^+$  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  $\text{Ga}^+$   
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  $\text{H}_3\text{BO}_3$  ( $4 \times 10^{-3} \text{ mol l}^{-1}$  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.

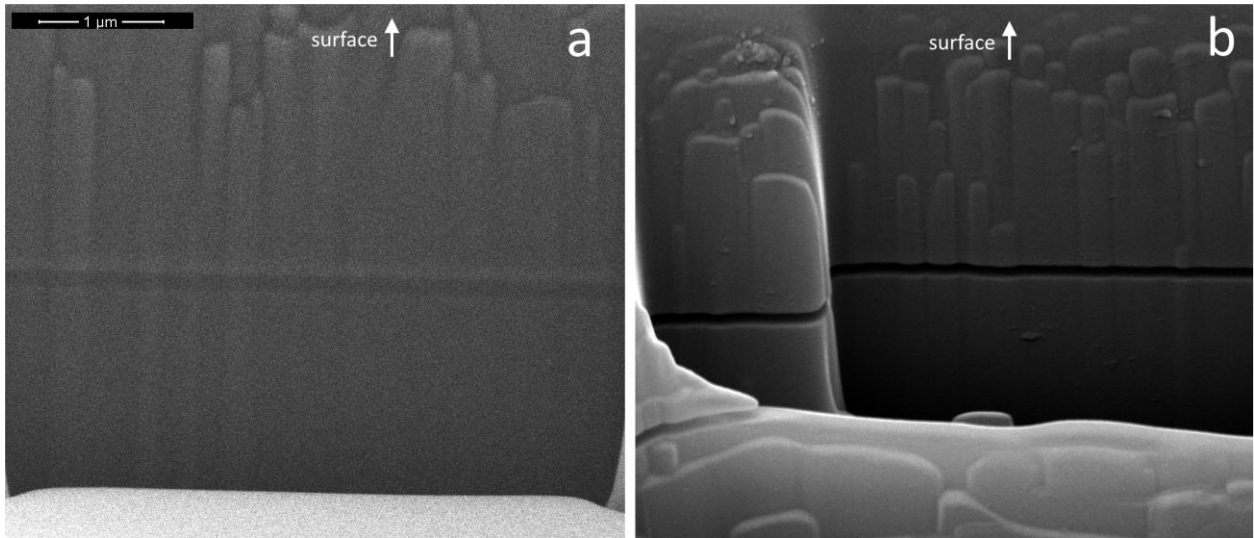
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### 161 **3. Results and discussion**

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

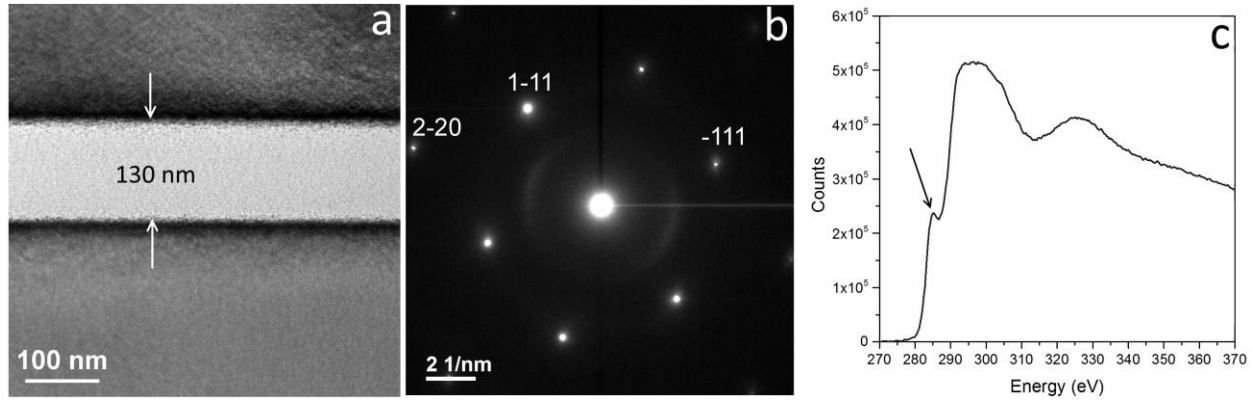
174 Fig. 2: Cross-sectional SEM micrographs of the sub-superficial graphitic layer in ion-implanted and annealed  
175 diamond a) before and b) after the selective etching process. A better definition of the geometrical parameters of the  
176 buried structure is clearly obtained after its selective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

177

178 The thickness of the buried layer evaluated from Fig. 2a is  $(200 \pm 40)$  nm, while it was estimated  
179  $(140 \pm 20)$  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  $(130 \pm 3)$  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  $\sim 285$  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.

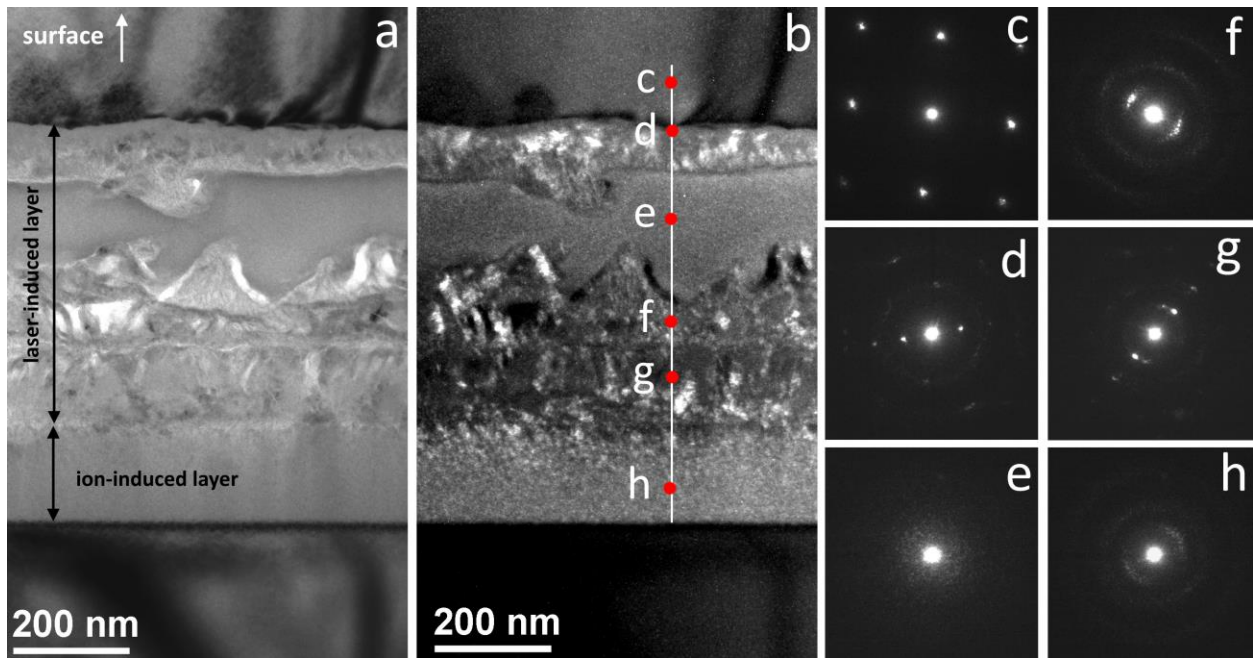


193  
 194 Fig. 3: a) Bright-field TEM cross-section micrograph of the sub-superficial graphitic layer in diamond before laser  
 195 irradiation (the sample surface is located towards the top of the picture). The thickness of the ion-implanted and  
 196 subsequently annealed structure is highlighted, corresponding to  $(130 \pm 3)$  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  $0.41 \text{ GW cm}^{-2}$  and  $0.45 \text{ GW cm}^{-2}$ ) 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  $0.41 \text{ GW cm}^{-2}$  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  $(690 \pm 15)$  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  $0.41 \text{ GW cm}^{-2}$ , 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].

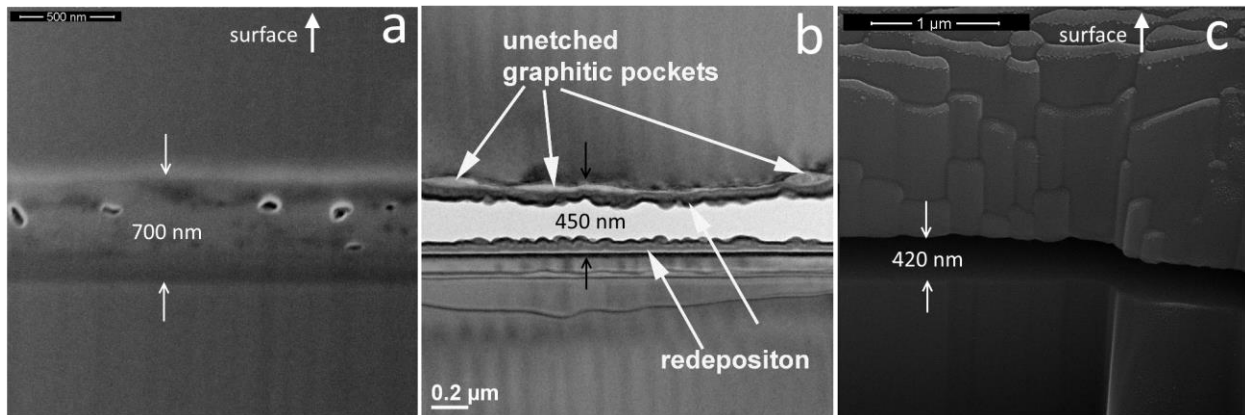
244 A SEM micrograph of the same laser-irradiated region is reported in Fig. 5a, from which a layer  
245 thickness of  $(700 \pm 70)$  nm can be estimated, compatibly (although with lower accuracy) with  
246 what obtained from TEM imaging. The amorphous areas are visible inside the graphitic layer, 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  $(420 \pm 20)$  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.

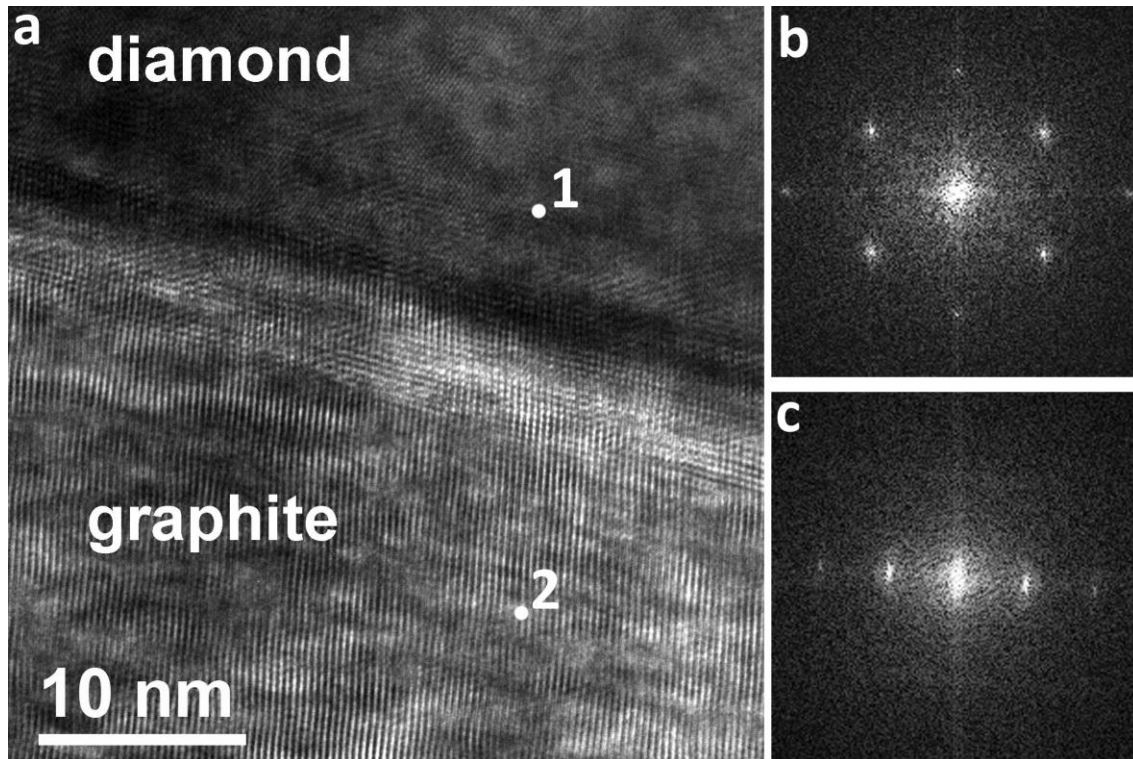


271  
 272 Fig. 5: a) Cross sectional SEM micrograph of the buried damaged layer after laser irradiation ( $\lambda = 532$  nm, power  
 273 density:  $0.41 \text{ GW cm}^{-2}$ , 50 pulses). b) Cross-sectional TEM micrograph of the same layer reported in a) after  
 274 electrochemical etching; together 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  $900^\circ\text{C}$  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.

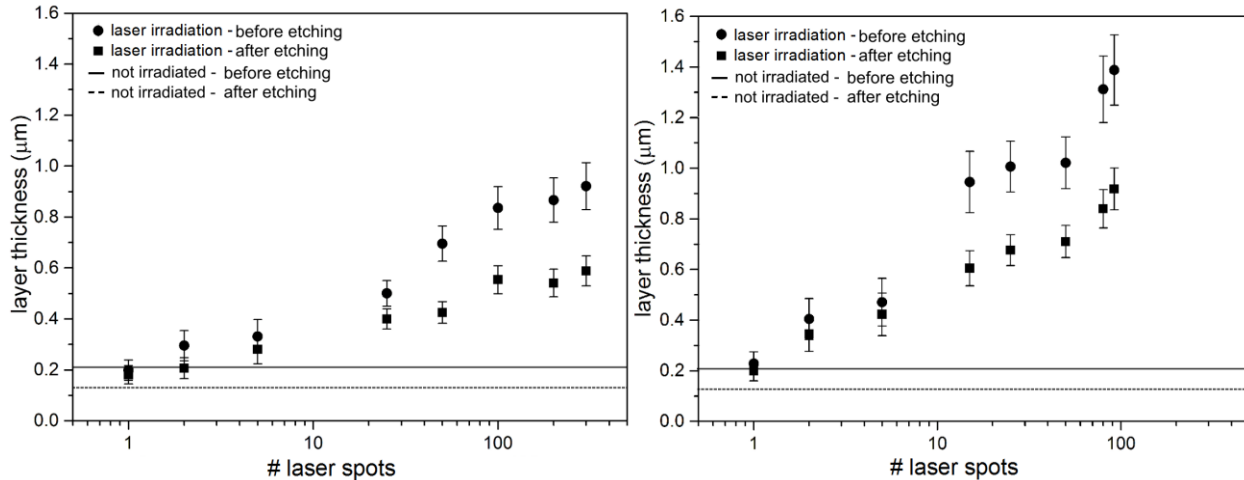
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290 The results reported so far refer to regions of the sample which were exposed to 50 laser pulses  
291 and subsequently subjected to different annealing and/or etching processes. A systematic  
292 investigation of the laser-induced graphitization 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  $0.41 \text{ GW cm}^{-2}$  and  $0.45 \text{ GW cm}^{-2}$  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  $\lambda = 532 \text{ nm}$  laser  
 319 pulses for two different power densities, i.e. a)  $P = 0.41 \text{ GW cm}^{-2}$  and b)  $P = 0.45 \text{ GW cm}^{-2}$ . 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  $\lambda = 532 \text{ nm}$  laser irradiation on the thickening of  
 326 sub-superficial graphitic layers in diamond obtained by means of  $2 \text{ MeV He}^+$  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  $900 \text{ }^\circ\text{C}$ , 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

#### 342 **Acknowledgments**

343 The authors wish to thank Genny Giaccardi for the kind support during laser processing. This  
344 work is supported by the following projects: "DiNaMo" (young researcher grant, project  
345 n° 157660) by National Institute of Nuclear Physics (I); FIRB "Futuro in Ricerca 2010" (CUP  
346 code: D11J11000450001) funded by MIUR and "A.Di.N-Tech." (CUP code:  
347 D15E13000130003), "Linea 1A - ORTO11RRT5" projects funded by the University of Torino  
348 and "Compagnia di San Paolo". Nanofacility Piemonte is laboratory supported by the  
349 "Compagnia di San Paolo" foundation.

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351 **References**

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