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Softening the ultra-stiff: Controlled variation of Young's modulus in single-crystal diamond by ion implantation

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Abstract

A combined experimental and numerical study on the variation of the elastic properties of defective single-crystal diamond is presented for the first time, by comparing nano-indentation measurements on MeV-ion-implanted samples with multi-scale modeling consisting of both *ab initio* atomistic calculations and meso-scale Finite Element Method (FEM) simulations. It is found that by locally introducing defects in the $2 \times 10^{18} - 5 \times 10^{21} \text{ cm}^{-3}$ density range, a significant reduction of Young's modulus, as well as of density, can be induced in the diamond crystal structure without incurring in the graphitization of the material. *Ab initio* atomistic simulations confirm the experimental findings with a good degree of confidence. FEM simulations are further employed to verify the consistency of measured deformations with a stiffness reduction, and to derive strain and stress levels in the implanted region. Combining these experimental and numerical results, we also provide insight into the mechanism responsible for the depth dependence of the graphitization threshold in diamond. This work prospers the possibility of achieving accurate tunability of the mechanical properties of single-crystal diamond through defect engineering, with significant technological applications, i.e. the fabrication and control of the resonant frequency of diamond-based micromechanical resonators.

Keywords : Diamond, Micro-/nanoindentation, Mechanical properties, Ion irradiation, *Ab initio* calculation, Finite Element Modeling

45

1. Introduction

46 Diamond is an extremely attractive material for a broad range of technological
47 applications due to its unique physical and chemical properties. In particular with regards to
48 its extreme mechanical and thermal properties, in the past years several works were focused
49 on developing mechanical structures and resonators in diamond either by MeV ion
50 implantation [1, 2] or by reactive ion etching [2-6] with the purpose of taking advantage of its
51 high mechanical hardness, stiffness and thermal conductivity. Moreover, diamond hosts a
52 wide variety of luminescent defect centres [7, 8] that can act as stable single photon emitters
53 at room temperature or as optically addressable solid-state spin-qubits [9, 10]. A challenging
54 goal in this field is to efficiently couple negatively charged nitrogen-vacancy centres to
55 resonant mechanical structures [11-13]. For advanced applications in nano-opto-mechanical
56 devices, the prospect of being able to modify and finely tune the mechanical properties of
57 diamond is therefore particularly appealing. In the case of other “2-D” carbon-based
58 materials (e.g. carbon nanotubes or graphene), the effect of structural defects on their
59 macroscopic mechanical properties has been studied both experimentally [14, 15] and
60 theoretically [16, 17], while a significant gap is present in the case of bulk diamond. Here, we
61 report such a systematic study, showing that a controlled modulation of the Young’s modulus
62 of diamond can be effectively achieved by defect engineering through MeV ion irradiation.
63 Ion beam lithography based on MeV [18-20] or keV ions [21, 22] has emerged in the past
64 years as one of the most promising techniques used in the micro- and nano-machining of
65 diamond for different applications. It is known that ion implantation induces structural
66 modifications (at low damage densities, consisting primarily of vacancies and interstitials
67 [23]) and local mass density variations in the diamond crystal, which in turn result in
68 mechanical deformations, including surface swelling [24] and local stresses [25, 26]. A
69 mixed analytical/numerical approach to estimate these stresses has been developed, providing

70 good agreement with experimental measurements [27]. One important issue that remains to
71 be adequately addressed, however, is the variation of the elastic properties of damaged
72 diamond as a function of induced damage density. This is particularly relevant for the
73 Young’s modulus, which is expected to vary between that of pristine diamond (i.e. ~1135
74 GPa [28, 29]) and that of amorphous carbon (i.e. ~20 GPa in a fully amorphized phase [30]).
75 Clearly, this large variation in elastic properties is likely to strongly affect the modeling of
76 implantation-induced stresses. Attempts have been made to experimentally derive the
77 variation of elastic properties in irradiated diamond [26], but only indirect estimations with
78 limited accuracy were obtained. This significant lack of experimental evidence is partly due
79 to the extremely high Young’s modulus value of the pristine material, which makes it
80 difficult to probe its mechanical properties. A related open question is represented by the
81 relatively high uncertainty found in the literature on the value of the so-called “amorphisation
82 threshold” of diamond, i.e. the damage level (usually parameterized with a vacancy density,
83 as calculated via the SRIM Monte Carlo code [31]) above which the diamond lattice is
84 permanently amorphized, and subsequently graphitizes upon thermal annealing. It is often
85 hypothesized that the large variability of this parameter is related to the depth of implantation
86 [32], as well as to self-annealing effects [33], but so far no unequivocal evidence of these
87 effects has been provided.

88 In this work we present the first systematic study of the controlled variation of the
89 elastic properties of diamond as a function on induced structural damage. The experimental
90 measurements of the Young’s modulus of MeV-ion-implanted diamond are performed with
91 the nano-indentation technique and results are complemented by numerical simulations at
92 two different scales, i.e. *ab initio* atomistic calculations of defected diamond supercells and
93 Finite Element Method (FEM) simulations of full-field deformations and stresses at the
94 meso-scale. Besides allowing a new level of control in the fine-tuning of mechanical

95 properties of diamond-based mechanical structures, our analysis also allows a novel
96 interpretation for the depth dependence of the amorphization threshold based on rigorous
97 continuum mechanics considerations.

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2. Experimental

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2.1. Sample preparation

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The sample under investigation was an artificial HPHT type Ib single crystal diamond sample synthesized by Sumitomo (Japan), $3\times 3\times 0.3$ mm³ in size, cut along the (100) crystalline direction with four optically polished faces: two opposite large surfaces and two opposite lateral surfaces. These “mechanical grade” diamond samples typically contain various impurities (N, Fe, Ni, Co) at concentration levels of the order of ~10-100 ppm, which do not affect significantly their mechanical properties, as confirmed by the test measurement performed from undamaged regions. The sample was implanted at room temperature on one of its lateral polished faces across its edge with one of its large surfaces, as schematically shown in Fig. 1, using a 2 MeV H⁺ ion microbeam at the INFN Legnaro National Laboratories. A rectangular area of approximately 100×200 μm² was raster-scanned to deliver a uniform implantation fluence of 1×10^{17} cm⁻².

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SRIM simulations were carried out using the SRIM 2012.03 Monte Carlo code [31] to estimate the linear damage profile $\lambda(x)$, expressed as the number of induced vacancies per incoming ion per unit depth x . The calculations were carried out in “Detailed calculation mode with full damage cascade” mode, by setting the atom displacement energy value to 50 eV [34]. According to simulations, the irradiation conditions generate a strongly inhomogeneous damage density profile peaked at a depth of ~25 μm from the surface (see the inset of Fig. 1).

119

120 *2.2. Raman characterization*

121 Micro-Raman spectroscopy was employed to assess the degree of
122 amorphization/graphitization in the regions of the diamond sample which were characterized
123 by the highest ion-induced damage density, i.e. in correspondence with the end-of-range
124 Bragg peak. The measurements were performed in the same cross-sectional geometry
125 adopted for the nanoindentation measurements, i.e. the probing laser beam was focused
126 across the upper surface of the sample and scanned across the ion-beam-induced damage
127 profile (see Fig. 1). A similar approach has been adopted in previous Raman studies in ion-
128 implanted diamond [32, 35]. An inVia Raman micro-spectrometer (Renishaw) was employed,
129 with a $\lambda = 514$ nm excitation laser beam focused onto a micrometric spot with a 80× objective.
130 The laser power focused on the probed region was ~2.5 mW. A PC-controlled stage allowed
131 the sample displacement across the three directions, and thus the mapping of the Raman
132 signal with micrometric resolution. Results are reported in Section 4.1.

133

134 *2.3. Nanoindentation measurements*

135 The lateral implantation geometry shown in Fig. 1 enabled to gain access to the upper
136 surface of the sample with a nano-indentation profilometer, and thus a direct measurement of
137 the structural and mechanical properties (i.e. hardness and Young’s modulus) of the damaged
138 diamond for a varying vacancy density profile. The choice of energetic light ions offered the
139 advantage of inducing a relatively broad damage profile, so that the nanoindentation
140 measurements were not influenced by edge effects. The nanoindentation measurements were
141 carried out with a Hysitron TI 950 TriboIndenter, allowing high spatial resolution down to
142 500 nm and the probing of ultra-hard materials such as diamond thanks to the large applied
143 loads 5000 μ N. The instrument is equipped with *in situ* Scanning Probe Microscopy (SPM)

144 imaging capability, using a Berkovich tip. The first step of the measurement consisted in the
145 acquisition of a large-area SPM topography map, to determine the location of the Bragg peak
146 and the corresponding swelling [36]. A Scanning Probe Microscopy (SPM) mapping of the
147 measured region is shown in Fig. 2(a), highlighting a line along which a profile was acquired,
148 from the sample edge to the bulk. The topography maps were acquired using the nano-
149 indenter Berkovich tip in contact mode with a set-point of 2 μN and with scan rate of 1 Hz,
150 and a scan size of $50 \times 50 \mu\text{m}^2$. A profile related to an unimplanted region near the indentation
151 line was subtracted from the SPM curves, to eliminate effects related to sample tilt, thermal
152 drift and nonlinearity of piezo-electric actuators. A $20 \times 20 \mu\text{m}^2$ map was then acquired in the
153 proximity of the peak and nano-indentation was performed in the same region. The
154 indentation profile was realized with 72 indents at a distance of 250 nm, resulting in a total
155 profile length of 18 μm . A load of 5 mN was applied at a rate of 0.5 mN s^{-1} , applying the
156 maximum load for each indentation for 2 s. In correspondence of every indent, “load vs
157 displacement” curves were acquired, from which the elastic modulus of the material was
158 derived using the approach proposed by Oliver and Pharr [37]. Indentation measurements
159 were performed in the linear elastic range, both in unimplanted and in ion-implanted areas.
160 As an example, Fig. 2(b) reports loading and unloading force-displacement curves collected
161 from unimplanted (dashed black curve) and implanted (solid blue curve) regions of the
162 sample, with the latter measurement taken in correspondence with the implantation Bragg
163 Peak. Loading and unloading curves coincide, showing that test are carried out in the linear
164 elastic range. Measurements were performed with a set-point of 2 μN and a loading rate of
165 500 $\mu\text{N/s}$. The measured reduced modulus E_r is related to the indenter and sample Young’s
166 moduli and Poisson’s ratios (E_i, ν_i) and (E_s, ν_s) , respectively, by the relation
167 $1/E_r = (1 - \nu_i^2)/E_i + (1 - \nu_s^2)/E_s$ which is derived from contact mechanics [37], with $E_i = 1140$
168 GPa and $\nu_i = 0.07$. In our case, both indenter and substrate were diamond, albeit with

169 different defect densities, so that they contributed to the reduced modulus in approximately
170 equal proportions. In order to obtain a direct comparison between indentation and topography
171 profiles, a SPM map of the region of interest was preliminarily acquired and four indentation
172 measurements were performed at its corners. SEM analysis performed on the tip before and
173 after the indentation revealed that no wear phenomena occurred during the tests. Results are
174 reported in Section 4.2

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3. Modelling

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3.1. *Ab initio* simulations

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An atomistic approach was employed to simulate the damage-induced modification of the Young's modulus in the material from first principles. For this purpose, the quantum-mechanical *ab initio* code CRYSTAL14 [38, 39] was employed, which allows the prediction of the structural and elastic properties of a defected material [40] through a “supercell” approach [41]. In this context, a supercell is a multiple of the unit cell that contains a vacancy at its body center. The CRYSTAL software creates a bulk system by the repetition of such a defective supercell, so that (contrary to the real physical system) the modeled system under investigation is homogeneous, i.e. defects are periodically distributed in the crystal. Supercells of different sizes allowed to simulate different defect densities. As shown in Fig. 3, single-defect cells with 128, 64, 32, 16 and 8 atoms were simulated, corresponding to vacancy densities of $1.4 \times 10^{21} \text{ cm}^{-3}$, $2.8 \times 10^{21} \text{ cm}^{-3}$, $5.5 \times 10^{21} \text{ cm}^{-3}$, $1.1 \times 10^{22} \text{ cm}^{-3}$ and $2.2 \times 10^{22} \text{ cm}^{-3}$. For each supercell, the geometry (both fractional coordinates and cell parameters) was first optimized. Then, the full elastic tensor was generated by deforming the unit cell. Second-order derivatives of the total energy with respect to the strain are evaluated in CRYSTAL as a numerical derivative of an analytical gradient [42, 43]. The Young's modulus was thus derived from the elastic constants tensor. Point symmetry was used at all

194 stages of the calculation to reduce the number of components of the elastic tensor to be
 195 considered. For each irreducible strain, a deformation was applied to the system, so that N
 196 strained configurations were defined according to a strain step. After a loop of N strained
 197 configurations, the energy gradients were fitted with single-value-decomposition routines and
 198 the first derivatives were determined numerically. Hartee-Fock (HF) and B3LYP
 199 Hamiltonians were adopted [44, 45], both of which have been shown to produce particularly
 200 accurate results for this kind of system [44], and the described procedure was adopted for
 201 both cases. The neutral vacancy in diamond can occur in three spin states, i.e. $S_z = 0, 1, 2$ [46,
 202 47]. The spin state of the defect was however found to have a negligible influence on the
 203 elastic properties, so that the reported data only refer to the $S_z = 0$ lowest-energy spin state.

204

205 *3.2. Mesoscale model*

206 The dependence of structural/mechanical properties of damaged diamond have
 207 previously been estimated using a phenomenological mesoscale model accounting for
 208 damage saturation effects at high fluences, based on a “rule of mixtures” approach [27].
 209 According to this model, when accounting for defect recombination in the crystal, the
 210 vacancy density ρ_V in the depth direction x can be expressed as:

211

$$212 \quad \rho_V(x) = \alpha \cdot \left(1 - \exp \left[- \frac{F \cdot \lambda(x)}{\alpha} \right] \right) \quad (1)$$

213

214 where $\lambda(x)$ is the linear vacancy density calculated numerically using the SRIM code, F is the
 215 implantation fluence and α is the saturation vacancy density. The latter α parameter can be
 216 derived as follows: let us consider an initial mass M and volume V_0 of diamond that after

217 implantation expands to a volume V containing n defects (i.e. vacancies), each assigned the
 218 same volume v for sake of simplicity. The vacancy density is therefore $\rho_V = n/V$. By
 219 neglecting the mass of the implanted ions, the mass density of the implanted diamond volume
 220 V is:

$$222 \quad \rho = \frac{M}{V} = \frac{M}{V_0 + nv} \quad (2)$$

223

224 Since $\rho_d = M/V_0 = 3.52 \text{ cm}^{-3}$ is the mass density of unimplanted diamond, we obtain:

225

$$226 \quad \frac{1}{\rho} = \frac{V_0 + nv}{M} = \frac{1}{\rho_d} + \frac{nv}{M} = \frac{1}{\rho_d} + \frac{nv}{\rho_d V} = \frac{1}{\rho_d} + \frac{\rho_V v}{\rho} \quad (3)$$

227

228 By rearranging, we obtain:

229

$$230 \quad \frac{\rho}{\rho_d} = 1 - \rho_V v = 1 - f \quad (4)$$

231

232 where $f = n \cdot v/V = v \cdot \rho_V$ is the volume fraction of vacancies, which correctly implies that $\rho = \rho_d$
 233 for $f = 0$, and $\rho = 0$ for $f = 1$. In fact, in our case an upper bound exists for f due to defect
 234 recombination effects [24] corresponding to a vacancy density saturation value $\rho_V = \alpha$. This
 235 vacancy density saturation value corresponds to an experimentally determined mass density
 236 saturation value of $\rho_{aC} = 2.06 \text{ g cm}^{-3}$ [48]. By rearranging Eq. (4) and estimating v as the
 237 inverse of the atomic density of diamond ($\gamma = 1.77 \times 10^{23} \text{ cm}^{-3}$), we can derive α as:

238

$$\alpha = \gamma \left(1 - \frac{\rho_{ac}}{\rho_d} \right) \approx 7.3 \cdot 10^{23} \text{ cm}^{-3} \quad (5),$$

240

241 consistently with previous works on 2 MeV H⁺ implantations [49]. This vacancy density is
 242 shown in the inset of Fig. 1. The mass density variation $\rho(x)$ can thus be written as:

243

$$\rho(x) = \rho_d - (\rho_d - \rho_{ac}) \cdot \left(1 - \exp \left[- \frac{F \cdot \lambda(x)}{\alpha} \right] \right) \quad (6)$$

245

246 The Young’s modulus dependence from the vacancy density can be derived from Quantized
 247 Fracture Mechanics (QFM) [17, 50] for the case of single isolated (non-interacting)
 248 vacancies:

249

$$E(x) = E_d \cdot \left(1 - \kappa \frac{\rho(x)}{\rho_d} \right) \quad (7)$$

251

252 where κ is an empirical factor related to defect shape and interaction [17].

253

254 3.3. Finite Element simulations

255 Finite Element Model (FEM) simulations were carried out using the Structural
 256 Mechanics module of the COMSOL Multiphysics 5.0 package. A 3-D model of the
 257 implanted diamond sample was created and constrained expansion of the implanted diamond

258 region due to local density reduction was simulated. The latter was numerically modelled
 259 according to elasticity theory by introducing residual strains $\varepsilon_i(x)$ in the three principal
 260 directions of the implanted material ($i = 1, 2, 3$):

261

$$262 \quad \varepsilon_i(x) = \sqrt[3]{\frac{\rho_d}{\rho(x)}} - 1 \quad (8)$$

263

264 In this way, in an unconstrained expansion the volume variation would be inversely
 265 proportional to the density variation. The diamond sample was considered mechanically
 266 isotropic as a first approximation. Material density and Young’s modulus spatial variations
 267 were accounted for using Eqs. (6) and (7). The same functional form, based on a rule of
 268 mixtures approach, was assumed for the variation of the Poisson’s ratio:

269

$$270 \quad \nu(x) = \nu_d - (\nu_d - \nu_{ac}) \left(1 - \exp \left[-\frac{F \cdot \lambda(x)}{\alpha} \right] \right) \quad (9)$$

271

272 where $\nu_d = 0.07$ and $\nu_{ac} = 0.34$ are the Poisson’s ratios of pristine diamond and amorphous
 273 carbon, respectively [51].

274

275

4. Results and discussion

276

4.1. Raman measurements

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Figure 4(a) shows several Raman spectra acquired across the end-of-range depth, the
 blue plot corresponding to the end-of-range position ($\sim 25 \mu\text{m}$). In the region characterized by
 the highest damage density a significant decrease of the first-order Raman line at 1332 cm^{-1} is

280 clearly observed which is associated to increasing structural damage, while no pronounced
281 Raman features at $\sim 1630\text{ cm}^{-1}$ and 1680 cm^{-1} (typically attributed to sp^2 defects [32, 52, 53])
282 can be observed. On the other hand, at frequencies lower than the 1st order transition, a broad
283 band between 1000 cm^{-1} and 1300 cm^{-1} appears at the highest damage densities (blue plot),
284 which is commonly attributed to sp^3 defects and in heavily stressed diamond [53, 54]. As for
285 the features at frequencies above the first order transition, it is worth noting that the Raman
286 peak at $\sim 1370\text{ cm}^{-1}$ closely resembles the D band at $\sim 1350\text{ cm}^{-1}$ commonly associated to
287 tetrahedral amorphous carbon characterized by a high sp^3 content [55], while no G band at
288 $\sim 1580\text{ cm}^{-1}$ is observed in our spectra. More likely, the $\sim 1370\text{ cm}^{-1}$ feature can be related
289 (with a slight frequency shift attributed to the effect of different local stress fields) to a
290 feature observed at $\sim 1390\text{ cm}^{-1}$ in highly stressed diamond regions close to laser-induced
291 graphitized areas, which was attributed to sp^3 carbon allotropes (i.e. Z-carbon and hexagonal
292 diamond) subjected to high mechanical stress [56]. A detailed analysis of the obtained Raman
293 spectra is beyond the scope of this work, but it is nonetheless worth remarking that all of the
294 above-mentioned attributions are compatible with a purely- sp^3 diamond-like phase, thus
295 confirming that even in correspondence with the Bragg peak the damaged diamond structure
296 is not subjected to a graphitization process. The progressive reduction of the first-order
297 Raman transition is accompanied by its broadening and shift to lower frequencies. The latter
298 feature is reported in Fig. 4(b), where the peak frequency is reported. The first-order Raman
299 peak corresponding to the Bragg peak is positioned at $\sim 1321\text{ cm}^{-1}$. In [32], the redshift of the
300 first-order Raman line in defective diamond has been correlated to vacancy density, estimated
301 by the authors in a simple linear approximation as the product between the linear vacancy
302 density predicted by SRIM and the implantation fluence. If such a correlation is applied to the
303 measured $\sim 1321\text{ cm}^{-1}$ value, an estimated vacancy density at the Bragg peak of $\sim 4.5 \times 10^{21}\text{ cm}^{-3}$
304 is obtained in the above-mentioned linear approximation. If we consider that the SRIM-

305 predicted linear vacancy density in such region is $\sim 4.5 \times 10^4 \text{ cm}^{-1}$, we can obtain an estimation
306 of the implantation fluence of $(4.5 \times 10^{21} \text{ cm}^{-3}) / (4.5 \times 10^4 \text{ cm}^{-1}) = 1 \times 10^{17} \text{ cm}^{-2}$, in striking
307 agreement with the corresponding experimental value. Again, these correspondences confirm
308 that the highly damaged regions of the sample can be still considered as a highly defective sp^3
309 diamond phase rather than a graphitized phase.

310

311 *4.2. Nanoindentation results*

312 Firstly, an unimplanted region of the sample was probed with the nano-indenter,
313 yielding a value of $E_r = (600 \pm 45) \text{ GPa}$ for the reduced Young’s modulus, which is
314 compatible with values from the literature [28, 29]. This measured reduced modulus value
315 corresponds to an effective Young’s modulus of $\hat{E} = E_s / [(1 - 2\nu_s) \cdot (1 + \nu_s)] = (1253 \pm 90)$
316 GPa, which can be used to write the relations between principal stresses σ_{ii} and strains ε_{ii} in
317 the generalized form of Hooke’s law in 3D [57].

318 For the implanted diamond regions, we exploited the nanometric spatial resolution of
319 the instrument (encoded to a resolution of 500 nm), allowing the investigation of the strongly
320 inhomogeneous damage profile in implanted diamond in correspondence with the end-of-
321 range Bragg peak (i.e. between 3 μm and 4 μm), where the variations in damage density and
322 stiffness are more pronounced. Cross-sectional SPM topography and elastic modulus profiles
323 of the implanted area, acquired from linear scans, are reported in Fig. 5: a $\sim 10\%$ decrease in
324 the value of the reduced modulus is clearly visible in correspondence of the surface swelling
325 peak. The position of the features along the depth direction match with the numerical
326 predictions of SRIM Monte Carlo code (see the inset of Fig. 1).

327

328 *4.3. Density/stiffness variations and surface swelling results*

329 Experimental and numerical results for the relative variation of mass density and
330 Young’s modulus as a function of vacancy density are presented in Figs. 6a and 6b,
331 respectively. For the mass density variation in Fig. 6a, the predictions of the model (see Eq.
332 (6)) are compared to the results of *ab initio* HF and B3LYP simulations, showing good
333 agreement and confirming the suitability of a model based on damage saturation effects. The
334 results of *ab initio* simulation of the Young’s modulus values were therefore fitted with Eq.
335 (7), allowing the determination of the empirical value $\kappa = 4.46$, which is close to the
336 reference value of $\kappa \approx \pi$ indicated in [17] for carbon nanotubes. The numerical predictions of
337 the Young’s modulus variation derived from both the model and the *ab initio* simulations
338 were then compared to experimental nanoindentation measurements, as reported in Fig. 6b.
339 Both predictions are compatible with the experimental data within their uncertainties,
340 although the theoretical predictions tend to systematically under-estimate the reduction in
341 Young’s modulus value. This tendency is confirmed by a previous experimental dataset from
342 [26] (also included in Fig. 6b), which also falls below numerical predictions. This systematic
343 underestimation by theoretical models can be reasonably attributed to the fact that in all of
344 the above-mentioned approaches only the effect of induced isolated vacancies is modelled,
345 while the possible effects of more complex defect aggregates are disregarded. Nonetheless,
346 the compatibility between theoretical and experimental results is striking, thus indicating that
347 (at least at the reported damage densities, i.e. below $\sim 10^{22}$ vacancies cm^{-3}) the isolated
348 vacancy defect indeed plays a major role in the modification of the mechanical properties of
349 diamond.

350 Finally, we verified the consistency of the QFM-based model with SPM
351 measurements of the damage-induced surface swelling by feeding its predictions of the local
352 variations of mass density (see Eq. (6) and Fig. 6a) and Young’s modulus (see Eq. (7) and
353 Fig. 6b) into the FEM simulation of the deformation of the ion-irradiated diamond region.

354 The results are shown in Fig. 7a: the calculated displacement field in the implanted area and
355 in the surrounding diamond crystal is visualized in colour scale, highlighting the localized
356 deformation that reaches a maximum on the top surface in correspondence with the Bragg
357 peak (see also Figs. 1 and 5). As shown in Fig. 7b, the calculated displacements agree very
358 well with the measured surface swelling, with the exception of the region extending beyond
359 the ion end of range depth at $\sim 25 \mu\text{m}$, where the theoretical predictions of the surface
360 swelling overestimate the experimental results. This is possibly due to the isotropic (instead
361 of cubic) symmetry used in FEM simulations for both implanted and unimplanted diamond:
362 such an approximation is more appropriate for the partially amorphized implanted material.
363 The SPM measurements show non-zero surface swelling effects ($\sim 22.5 \text{ nm}$) at the leading
364 edge of the implanted region, where the vacancy density is negligible, a feature correctly
365 captured by FEM simulations. Since the Young’s modulus variation used in the FEM
366 simulations is derived from QFM calculations with a κ interaction parameter derived from *ab*
367 *initio* simulations, the agreement between FEM-calculated and experimentally measured
368 surface displacements represents a significant confirmation of the consistency of obtained
369 results.

370 FEM simulations based on the predictions of multi-scale modelling of the variation of
371 the structural/mechanical properties in ion-implanted diamond can also provide reliable
372 estimates of locally induced strains and stresses, including in the bulk of the implanted
373 crystal, which is not accessible to direct measurements. This is essential when performing
374 diamond microfabrication, since it was recently shown that diamond amorphization is a
375 strain-driven process [48], i.e. it occurs in regions where a defined strain threshold ($\sim 16\%$) is
376 exceeded. Therefore, such a strain (or equivalently, stress) value must be estimated with the
377 highest accuracy. Here, as an example we report in Fig. 7c the Von Mises stress profiles
378 along the x direction (i.e. the direction of the incident ion beam), as calculated at three

379 different positions along the z axis, from the top surface ($z = 0 \mu\text{m}$) to the lower border of the
380 implanted region ($z = -h = -100 \mu\text{m}$). As expected, all stress profiles display a pronounced
381 peak at the end-of-range depth of the ions, where the defect density is largest, reaching values
382 of up to 12 GPa at the sample surface. Moreover, a 3-fold decrease of the end-of-range stress
383 value is observed at a depth of $\sim 100 \mu\text{m}$. This evidence provides significant insight into an
384 open issue in the state of the art, i.e. the depth dependence of the amorphization threshold for
385 diamond [23, 32, 33, 58-65]. The general (but so far undemonstrated) understanding is that
386 such a threshold increases at increasing implantation depth due to higher internal pressures
387 that do not allow relaxation to graphitic structures [32]. Here we show quantitatively that in
388 fact the opposite is true, i.e. deeper implants induce smaller stresses (and strains). This is
389 nevertheless consistent with experimental observations, i.e. higher defect densities are
390 required at increasing depths to achieve the same amorphization-inducing strain values. The
391 estimated 3-fold increase in amorphisation threshold for a $100 \mu\text{m}$ depth is consistent with
392 experimentally observed variations in the literature [23, 32, 33, 58-65].

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5. Conclusions

395 A systematic study of the variation of the structural and mechanical properties of
396 defected diamond was carried out with cross-sectional Raman, SPM and nano-indentation
397 measurements carried on MeV-ion-implanted samples. The experimental results display a
398 very satisfactory agreement with complementary *ab initio* atomistic and mesoscale models,
399 also when integrated in FEM simulations. Measurements show that a softening effect of up to
400 15% in diamond, i.e. the hardest known bulk material, can potentially be obtained in a
401 controlled manner using ion irradiation and/or FIB techniques without incurring in the full
402 amorphization/graphitization of the pristine crystal. Simulations predict that this effect can
403 reach nearly 50% for higher damage densities ($\sim 2.2 \cdot 10^{22} \text{ cm}^{-3}$), still lying below the

404 graphitization threshold for diamond ($\sim 2.8 \cdot 10^{22} \text{ cm}^{-3}$) [48]. The proposed approach opens the
405 way to the possibility of achieving a three-dimensional control and tuning of the Young’s
406 modulus of diamond with a micrometric spatial resolution by adopting advanced
407 microfabrication techniques, e.g. lateral irradiation configurations, multiple implantations,
408 and/or appropriate masking processes. Furthermore, this work demonstrates the possibility of
409 obtaining through FEM simulations an accurate mapping of the stress fields present in the
410 ion-damaged material, allowing for a useful control during various microfabrication stages.
411 Simulations show that deeper implants require a higher density of induced defects to promote
412 amorphization, confirming both the strain-driven mechanism proposed in previous works
413 [48] and the generally observed increase of the graphitization threshold for deeper ion
414 implantations [23, 32, 33, 58-65].

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List of Figure captions

Fig. 1: Schematic representation (not to scale) of the experimental configuration: MeV ion implantation (red arrow) was performed on a lateral polished surface. The corresponding damage profile derived from Eq. (2) is reported in the inset graph on the right. Scanning nano-indentation and SPM measurements were carried out on the upper surface of the sample.

Fig. 2: a) Scanning Probe Microscopy map of the region of interest. The line labeled as “1” shows a typical scan along which nanoindentation measurements were performed. The end-of-range peak (highlighted by a dotted line) is visible at about 25 μm from the surface. b) Force-displacement nanoindentation curves for implanted (continuous blue line) and unimplanted (dashed black line) regions of the diamond sample.

Fig. 3: Defected diamond unit cells considered in ab initio simulations, ranging from 128- to 8-atom systems with a single vacancy at their body centres.

Fig. 4: a) Micro-Raman spectra acquired across the highly damaged region; the spectra are displaced along the vertical axis for sake of readability; the blue spectrum corresponds to the Bragg peak region at the end of ion range; b) corresponding values of the shift of the first-order Raman peak measured at different positions across the sample depth; the highlighted datapoints correspond to spectra of the same color in a).

616 Fig. 5: SPM topography (blue circular dots, scale on the left) and Young’s modulus (red
617 square dots, scale on the right) depth profiles of the implanted area acquired along the same
618 linear scan in correspondence with the end-of-range Bragg peak.

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620 Fig. 6: a) mass density percentage reduction obtained as a function of vacancy density from
621 ab initio (blue diamond and red square dots for HF and B3LYP Hamiltonians, respectively)
622 and mesoscale (continuous black line) simulations; b) Young’s modulus percentage reduction
623 as a function of vacancy density obtained in nanoindentation experiments (black triangular
624 dots), from ab initio simulations using HF and B3LYP hamiltonians (blue diamond and red
625 square dots, respectively), from Quantum Fracture Mechanics calculations (continuous black
626 line) and from experimental data in the literature [26] (green circular dots).

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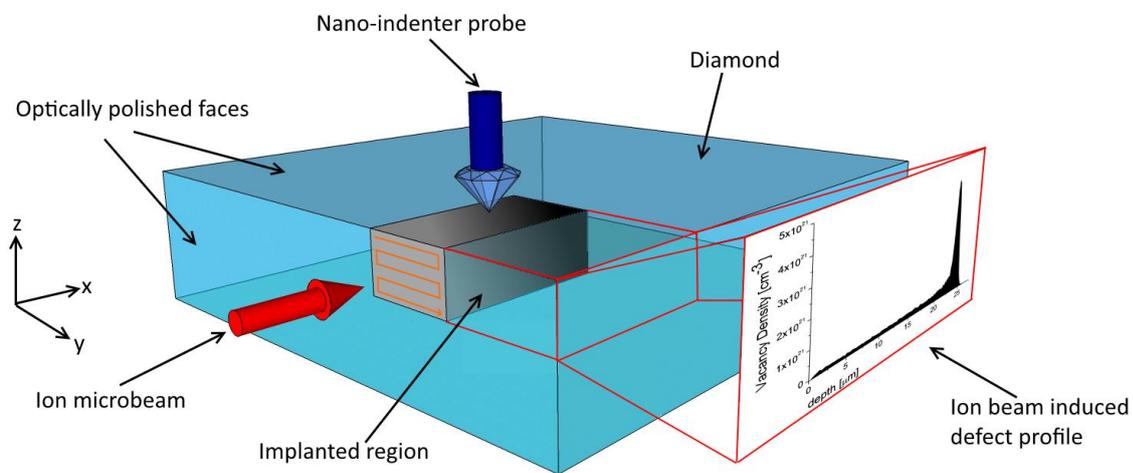
628 Fig. 7: a) FEM-simulated displacements (in colour scale) in a laterally implanted diamond
629 sample, on an area of height $h = 100 \mu\text{m}$. b) SPM topography and FEM simulations
630 representing the swelling effect over the whole ion penetration depth (left scale) and SRIM
631 vacancy density profile (right scale). c) Calculated Von Mises stress variation in the y
632 direction at three different depths from the sample surface: $z = 0 \mu\text{m}$, $-50 \mu\text{m}$ and $-100 \mu\text{m}$.

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Figure 1

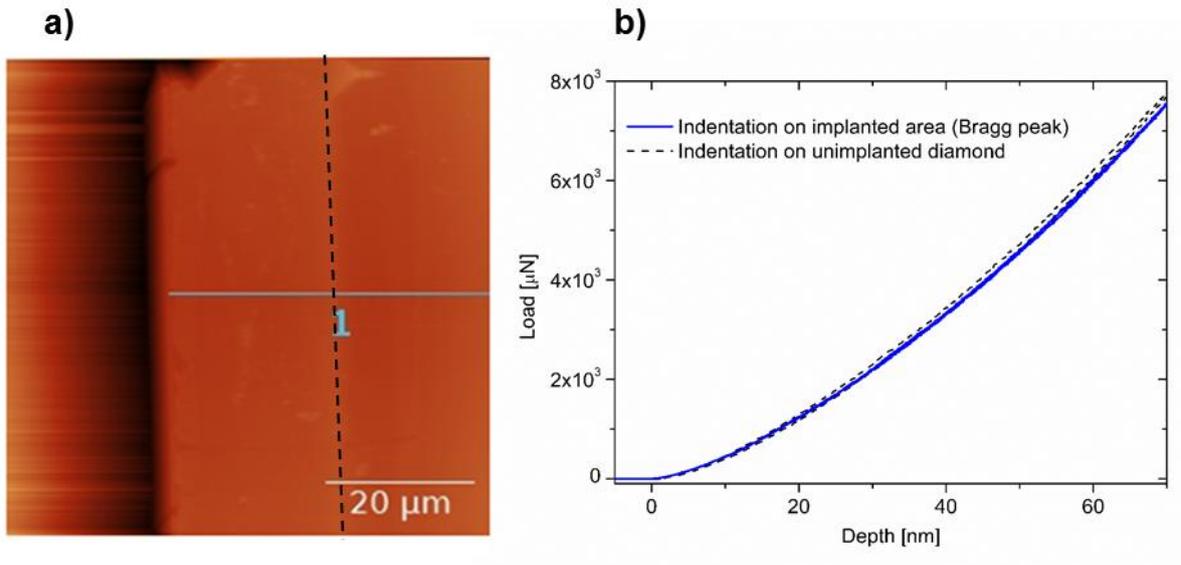


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Figure 2



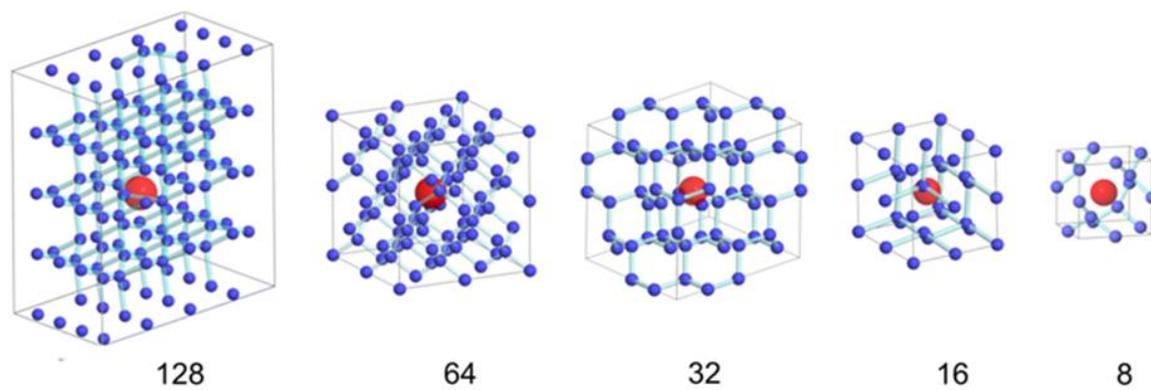
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Figure 3

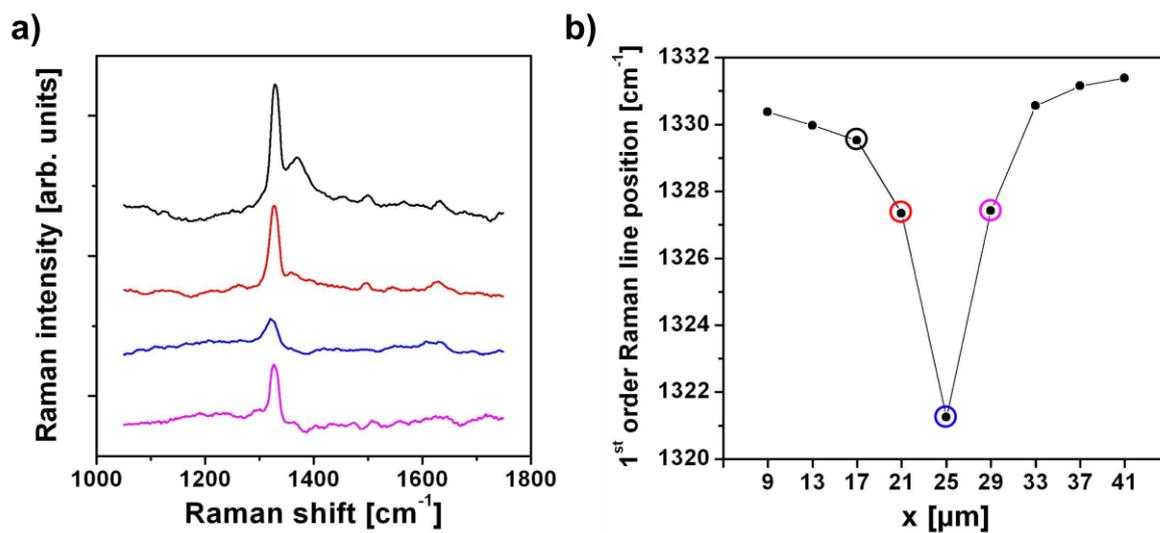


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Figure 4

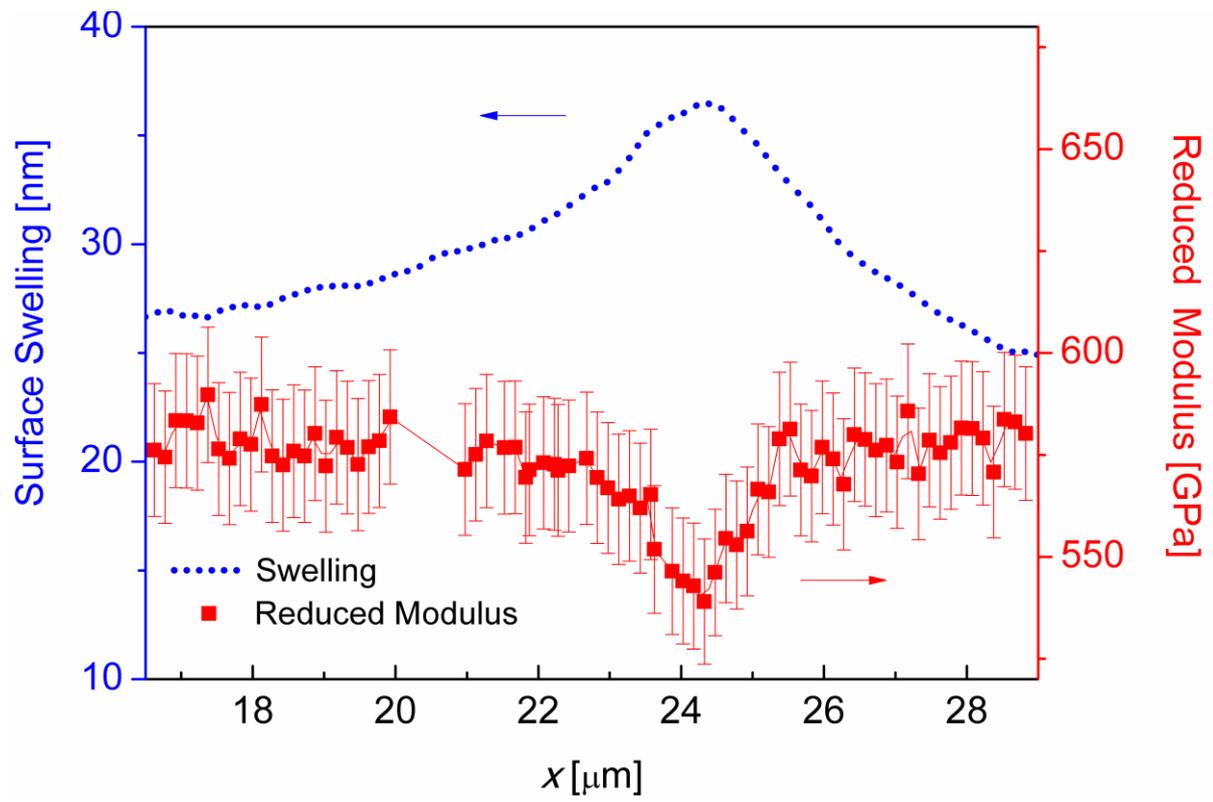


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Figure 5

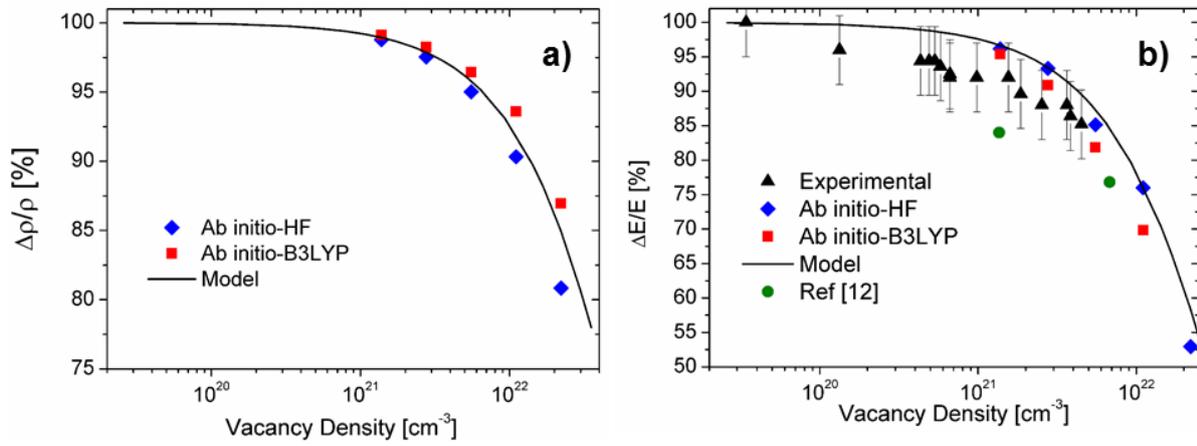


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Figure 6

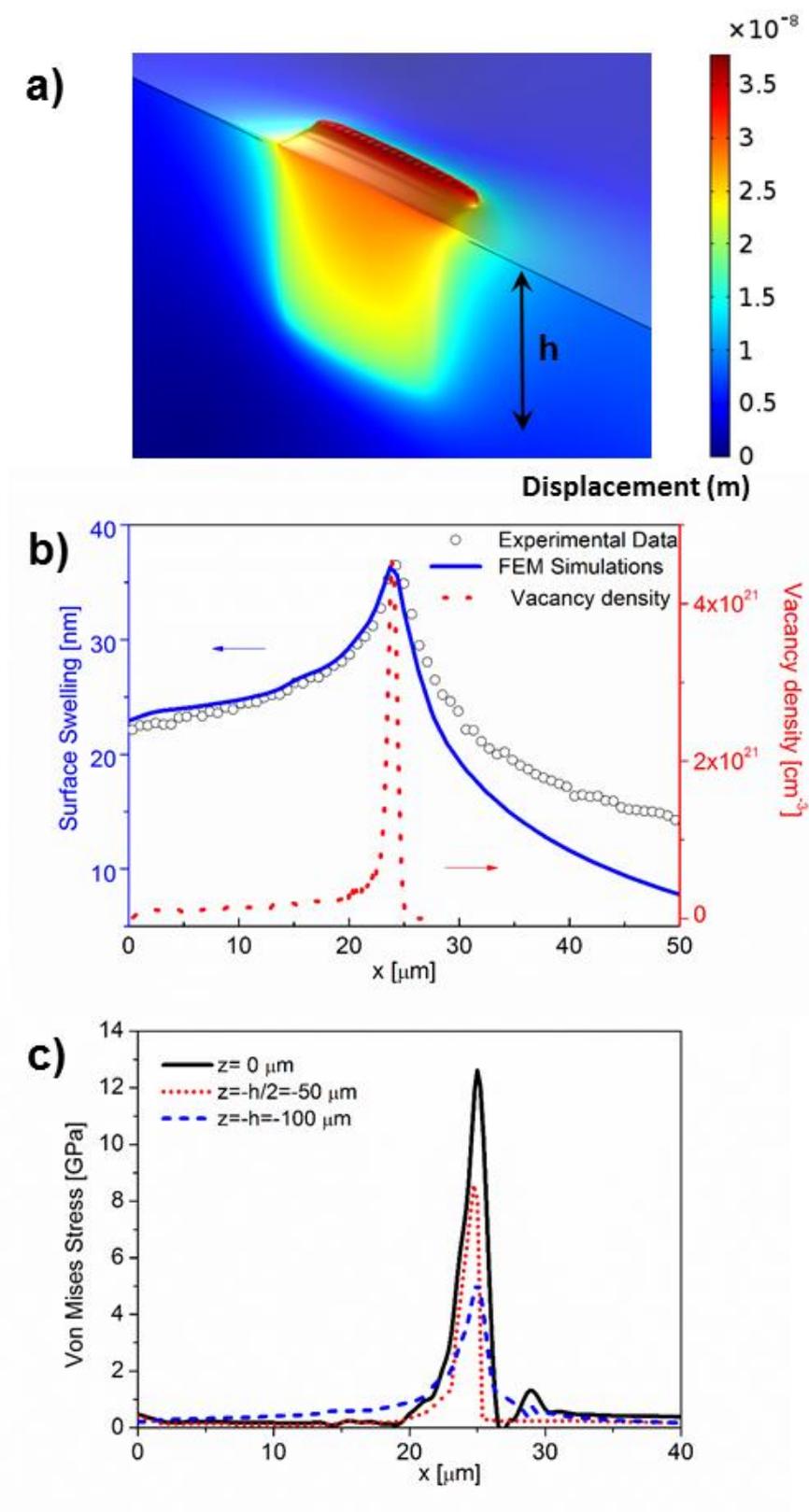


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Figure 7



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