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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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A B S T R A C T

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 2×10^{18}–5×10^{21} 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 prospects the possibility of achieving accurate tunability of the mechanical properties of single-crystal diamond through defect engineering, with significant technological applications, e.g. the fabrication and control of the resonant frequency of diamond-based micromechanical resonators.

1. Introduction

Diamond is an extremely attractive material for a broad range of technological applications due to its unique physical and chemical properties. In particular with regards to its extreme mechanical and thermal properties, in the past years several works were focused on developing mechanical structures and resonators in diamond either by MeV ion implantation [1,2] or by reactive ion etching [2–6] with the purpose of taking advantage of its high mechanical hardness, stiffness and thermal conductivity. Moreover, diamond hosts a wide variety of luminescent defect centres [7,8] that can act as stable single photon emitters at room temperature or as optically addressable solid-state spin-qubits [9,10]. A challenging goal in this field is to efficiently couple negatively charged nitrogen-vacancy centres to resonant mechanical structures [11–13]. For advanced applications in nano-opto-mechanical devices, the prospect of being able to modify and finely tune the mechanical properties of diamond is therefore particularly appealing. In the case of other carbon-based materials (e.g. carbon nanotubes, fullerenes or graphene), the effect of structural defects on their macroscopic mechanical properties has been studied both experimentally [14,15]

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and theoretically [16,17], while a significant gap is present in the case of bulk diamond. Here, we report such a systematic study, showing that a controlled modulation of the Young's modulus of diamond can be effectively achieved by defect engineering through MeV ion irradiation. Ion beam lithography based on MeV [18–20] or keV ions [21,22] has emerged in the past years as one of the most promising techniques used in the micro- and nano-machining of diamond for different applications. It is known that ion implantation induces structural modifications (at low damage densities, consisting primarily of vacancies and interstitials [23]) and local mass density variations in the diamond crystal, which in turn result in mechanical deformations, including surface swelling [24] and local stresses [25,26]. A mixed analytical/numerical approach to estimate these stresses has been developed, providing good agreement with experimental measurements [27]. One important issue that remains to be adequately addressed, however, is the variation of the elastic properties of damaged diamond as a function of induced damage density. This is particularly relevant for the Young's modulus, which is expected to vary between that of pristine diamond (i.e. ~1135 GPa [28,29]) and that of amorphous carbon (i.e. ~20 GPa in a fully amorphized phase [30]). Clearly, this large variation in the elastic properties is likely to strongly affect the modeling of implantation-induced stresses. Attempts have been made to experimentally derive the variation of elastic properties in irradiated diamond [26], but only indirect estimations with limited accuracy were obtained. This significant lack of experimental evidence is partly due to the extremely high Young's modulus value of the pristine material, which makes it difficult to probe its mechanical properties. A related open question is represented by the relatively high uncertainty found in the literature on the value of the so-called "amorphization threshold" of diamond, i.e. the damage level (usually parameterized with a vacancy density, as calculated via the SRIM Monte Carlo code [31]) above which the diamond lattice is permanently amorphized, and subsequently graphitizes upon thermal annealing. It is often hypothesized that the large variability of this parameter is related to the depth of implantation [32], as well as to self-annealing effects [33], but so far no unequivocal evidence of these effects has been provided.

In this work we present the first systematic study of the controlled variation of the elastic properties of diamond as a function on induced structural damage. The experimental measurements of the Young's modulus of MeV-ion-implanted diamond are performed with the nano-indentation technique and results are complemented by numerical simulations at two different scales, i.e. *ab initio* atomistic calculations of defected diamond supercells and Finite Element Method (FEM) simulations of full-field deformations and stresses at the meso-scale. Besides allowing a new level of control in the fine-tuning of mechanical properties of diamond-based mechanical structures, our analysis also allows a novel interpretation for the depth dependence of the amorphization threshold based on rigorous continuum mechanics considerations.

2. Experimental

2.1. Sample preparation

The sample under investigation was an artificial HPHT type Ib single crystal diamond sample synthesized by Sumitomo (Japan), $3 \times 3 \times 0.3$ mm^3 in size, cut along the (100) crystalline direction with four optically polished faces, i.e. 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 μm^2 was raster-scanned to deliver a uniform implantation fluence of 1×10^{17} cm^{-2}.

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).

2.2. Raman characterization

Micro-Raman spectroscopy was employed to assess the degree of amorphization/graphitization in the regions of the diamond sample which were characterized by the highest ion-induced damage density, i.e. in correspondence with the end-of-range Bragg peak. The measurements were performed in the same cross-sectional geometry adopted for the nanoindentation measurements, i.e. the probing laser beam was focused across the upper surface of the sample and scanned across the ion-beam-induced damage profile (see Fig. 1 as a reference). A similar approach has

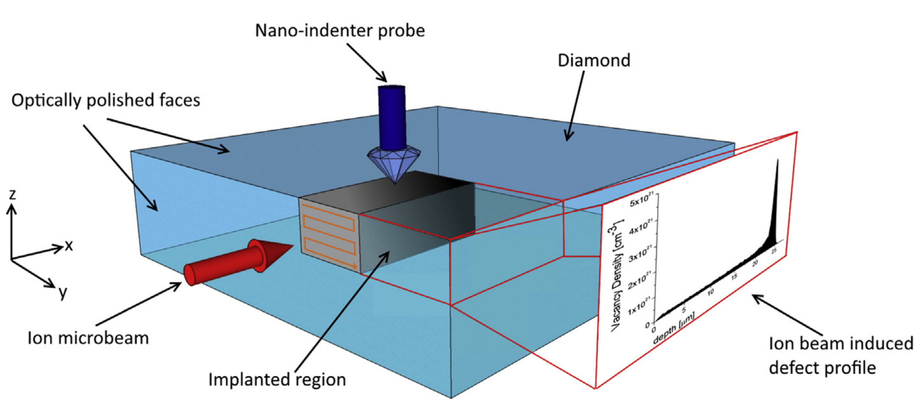

Fig. 1. Schematic representation (not to scale) of the experimental configuration: MeV ion implantation (red arrow) was performed on a lateral polished surface. The corresponding damage profile derived from Eq. (2) is reported in the inset graph on the right. Scanning nano-indentation and SPM measurements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