Experimental determination of Young's modulus reduction in ion implanted diamond

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INTRODUCTION

MeV ion implantation has been widely exploited in recent years for the micro-fabrication and functionalization of single crystal diamond [1]. Various works have shown that this technique can be effectively adopted to engineer the electrical, optical and structural properties of diamond [2-3]. The induced damage density can be controlled by varying implantation parameters, such as ion species and fluence, resulting in the formation of point defects (essentially vacancies and interstitials), in the amorphization and eventually in the permanent graphitization of the pristine crystal upon thermal annealing when a critical damage threshold is reached [4].

The use of microbeams has been particularly effective in exploiting this amorphisation process to create three-dimensional structures for specific applications e.g. in photonics [5] and biosensing [6], including buried graphitic electrodes, optical waveguides and microfluidic channels. It is known that mechanical deformation effects are associated to the structural variations occurring in the crystal due to ion implantation, including surface swelling effects, density and stiffness reductions that lead to stress concentrations at the borders of the implanted regions [7]. In particular, the amorphization/graphitization threshold has recently been shown to be strain-related, rather than damage related [8]. To reliably design and fabricate such complex structures in diamond, it is thus necessary to be able to predict deformation and stress levels with considerable accuracy. A phenomenological model to do this has been recently developed and validated after comparison with various different experimental data sets [9]. One issue that remains to be adequately addressed, however, is the variation of elastic properties of damaged diamond as a function of the implantation fluence, in particular that of its Young's modulus, which is expected to vary between that of pristine diamond (>1 TPa, in the presence of no damage) to that of amorphous carbon (~10 GPa, for full amorphization), i.e. by two orders of magnitude. Clearly this large variation in elastic properties is likely to strongly affect modeling results. Attempts have been made to experimentally derive the variation of elastic properties, e.g. in [10], but only indirect estimations with limited accuracy have been obtained. This lack of experimental data is partly due to diamond's extremely high values of Young's modulus (the stiffest known material, together with carbon nanotubes or graphene), which makes it difficult to perform indentation experiments. Here, we perform a systematic study of the elastic properties of ion implanted diamond by means of nano-indentation measurements.

ION BEAM IMPLANTATION

The sample under exam is a synthetic single crystal diamond produced by chemical vapour deposition. The diamond is 3×3×0.3 mm^3 in size, cut along the (100) crystalline direction with four optically polished faces: two opposite large faces and two opposite small faces. The crystal is classified type IIa having single substitutional nitrogen concentration below 1 ppm and single substitutional boron concentration below 50 ppb.

The sample was implanted at room temperature with a 2 MeV H^+ ion microbeam at the ion microscopy line of the AN2000 accelerator facility of the INFN Legnaro National Laboratories (INFN-LNL). A rectangular area was implanted with the fluence of $1 \cdot 10^{17}$ cm^{-2} on the small polished face in proximity of the edge between this face and the large one. This implantation geometry allows to measure the mechanical properties (i.e. Hardness and Young's modulus) of the damaged region at increasing ion penetration depth by means of a nano-indentation profilometer on the unimplanted polished face (see fig. 1).

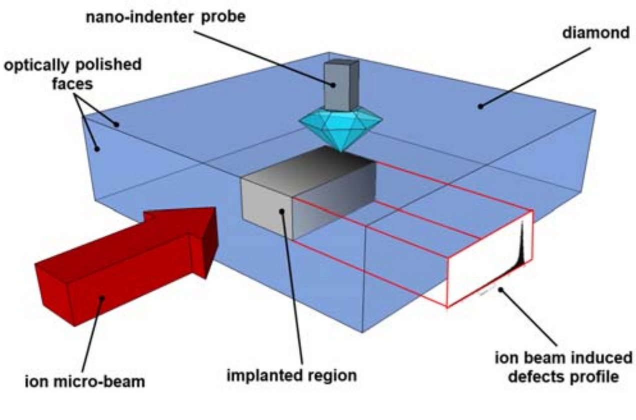

Fig. 1: Schematic of the experimental set up Nanoindentation measurements

Nanoindentation is an indentation test in which the length scale of the penetration is measured in nanometers. The distinguishing feature of most nanoindentation tests is the indirect measurement of the area between the indenter and the specimen (contact area). The contact area is determined by measuring the depth of penetration of the indenter into the specimen surface. Moreover, quasistatic nanoindentation has become the standard technique used for nanomechanical characterization of materials. A quasistatic nanoindentation test is performed by applying and removing a controlled load to a sample with a geometrically well-defined probe. During the nanoindentation test, a traditional force versus displacement curve is produced applying a force by the transducer and observing the resulting displacement. The analysis of these curve provide information regarding the mechanical properties of the sample. Values typically obtained from quasistatic nanoindentation tests are Hardness (H) and Reduced Modulus (E_r).

E_r is given by:

$$\frac{1}{E_r} = \frac{\left(1-\nu^2\right)}{E} + \frac{\left(1-\nu_i^2\right)}{E_i}\ ; \qquad (1)$$

E and υ are the elastic modulus and Poisson's ratio of the specimen, while E_i and υ_i are material constants for the indenter tip. This equation assumes that the deflection of the tip is zero, which is a reasonable assumption since the diamond tip is extremely rigid, with $E_i = 1.140$ GPa and $\upsilon_i = 0.07$, respectively.

In this work nanoindentation tests were carried out with an Hysitron instrument (TI 950 TriboIndenter), using a Berkovich tip. A Berkovich tip is a 3-sided pyramid with an included angle of 142.3°, where the angle from the normal to a face is 65.35°.

Profiles were realized at a distance of 5 µm, each profile was realized with 80 indents at a distance of 0.15 µm. A load of 5000 µN was applied with a rate of 500 µN s^{-1}, the maximum load for each indentation is applied for 2 s.

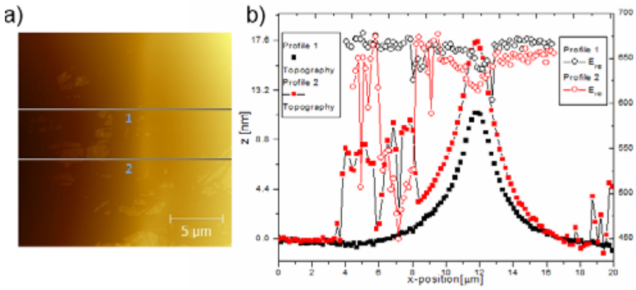

Fig. 2: (a) Scanning Probe Microscopy map of the region of interest; (b) Topography and Reduced Modulus profiles measured along the gray lines depicted in (a). The topography profiles are represented by black squares (profile 1) and red squares (profile 2). Reduced Modulus values are represented by black circles (profile 1) and red circles (profile 2).

RESULTS

Figure 2(a) shows the topography map of the diamond region on which nano-indentation measurements have been performed. This map has been acquired using the nanoindenter as a Scanning Probe Microscope. In figure 2 (a) the z-coordinate is represented with a colour scale: upper regions are characterized by a brighter colour, lower regions are characterized by a darker colour. The nanoindentation measurements have been performed along the two grey lines in the figure 2(a). The swelling localized at the implanted area appears in the figure as a bright area orthogonal to the grey lines. This is a well-know effect [11] due the lower density of the graphitic channel with respect to that of diamond.

In figure 2(b), red and black circles represent the values of Reduced Modulus collected along the two grey lines shown in figure 2(a). In both cases a minimum in the Reduced Modulus for the same x-position can be noted. These minima in Reduced Modulus are localized in the implanted area, as can be seen comparing Reduced Modulus profiles with topography profiles (red and black squares); in fact, the minima in Reduced Modulus and the maxima in topography (swelling) occur at the same x-position. The small differences of values obtained from the two profiles are due to the fact that profile 2 is in correspondence of the centre of the implanted area, while profile 1 is taken at the border of the implanted area.

The strong variation of both topography and Reduced Modulus in profile 2 at x-position around 6 µm derive from a contaminated surface layer. The values of Reduced Modulus far from the implanted area agree with the one of unimplanted diamond.

CONCLUSIONS

The preliminary results presented in this paper indicate that nanoindentation is an insightful technique to directly probe the elastic properties of ion implanted diamond. Future activities will be focused on the characterization of several areas implanted at different fluences.

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