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Micro and nano-patterning of single-crystal diamond by swift heavy ion irradiation

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ABSTRACT

This paper presents experimental data and analysis of the structural damage caused by swift-heavy ion irradiation of single-crystal diamond. The patterned buried structural damage is shown to generate, via swelling, a mirror-pattern on the sample surface, which remains largely damage-free. While extensive results are available for light ion implantations, this effect is reported here for the first time in the heavy ion regime, where a completely different range of input parameters (in terms of ion species, energy, stopping power, etc.) is available for customized irradiation. The chosen ion species are Au and Br, in the energy range 10–40 MeV. The observed patterns, as characterized by profilometry and atomic force microscopy, are reported in a series of model experiments, which show swelling patterns ranging from a few nm to above 200 nm. Moreover, a systematic phenomenological modeling is presented, in which surface swelling measurements are correlated to buried crystal damage. A comparison is made with data for light ion implantations, showing good compatibility with the proposed models. The modeling presented in this work can be useful for the design and realization of micropatterned surfaces in single crystal diamond, allowing generating highly customized structures by combining appropriately chosen irradiation parameters and masks.

1. Introduction

Structural damage induced in single-crystal diamond by ion irradiation has been studied in a variety of experimental configurations, which mostly include the use of medium/light ions at ~0.1–1 MeV energies for both fundamental studies [1–5] and device applications [6–9]. Remarkably, no systematic irradiation studies with swift heavy ion beams have been performed until very recently [10]. For all the data presented in this work, the damage generation mechanism can be attributed exclusively to nuclear stopping, since the electronic stopping force lies in the range below 14 keV/nm [2,3,10]. Due to the energy dependence of nuclear stopping, ion beams with high enough energy generate significant structural damage below the sample surface, whereas the surface layers undergo limited structural modifications. The length scales involved are typically in the micrometer range, both for the thickness of the undamaged surface layer and for that of the buried damaged one. The effect of the induced stress on the crystalline surface layer, generated by the expansion of the underlying damaged volume, gives rise to surface swelling, which has been observed and phenomenologically described in the light ion regime or at low ion energies [11–13].

The aim of this paper is twofold: firstly, to report the swelling effect in the swift heavy ion regime, comparing experimental results with the phenomenological model developed for light ions [12,13] in order to assess its validity also for swift heavy ions and, secondly, to highlight the potential exploitation of the swelling effect, with an extended range of input parameters offered by swift heavy ions of arbitrary species, to generate customized surface landscapes of lightly damaged diamond crystals with interesting aspect ratio characteristics. Phenomenological

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models are described in order to provide simple tools to fine-tune irradiation parameters to the desired surface effect in a customized way.

2. Swift heavy ion implantations

Optical-grade single-crystal diamond samples, $(3 \times 3 \times 0.3)\ \mathrm{mm}^3$ in size, (100) oriented and with two polished surfaces were supplied by ElementSix [14]. The samples were classified as type IIa, corresponding to concentrations of N and B impurities below 1 ppm and 50 ppb, respectively. Irradiations were performed at CMAM [15,16], using the standard beamline [17]. Samples were implanted in frontal geometry on their polished surfaces, with slight tilting in order to avoid channelling effects. The different ion beams employed were defocused so as to provide homogeneous irradiation of the whole sample surface. Homogeneity was carefully tested for each beam configuration by irradiating a test quartz sample and measuring the induced luminescence on a CCD camera.

The adopted beams included Au and Br ions, with energies in the range 10–40 MeV and fluences in the range from $5 \times 10^{13}\ \mathrm{cm}^{-2}$ to $5 \times 10^{14}\ \mathrm{cm}^{-2}$. During the corresponding irradiations, samples were masked with suitable grids, providing lateral 2D irradiation patterns to test the material response. Beam currents from a few tens of nA to 130 nA where used as available from the CMAM accelerator for the different ion species and energies chosen. The different experimental configurations are summarized in Table 1. The chosen ion species and energies are focused on a systematic study as a function of fluence and with different mask configurations for 10 MeV Au ions, complemented with a sample at higher Au beam energy and with a few samples irradiated with Br, exploring a lower nuclear stopping power range. Br irradiation parameters were chosen so as to provide some overlap with the information provided by Au irradiations, as discussed in Section 4 below.

The sample surface topography of as-irradiated samples was characterized by profilometry, used in this paper as the main characterization technique for systematic analysis of the swelling effect. The measurements were conducted at the Nanoquim Platform Laboratory at Institut de Ciència de Materials de Barcelona (ICMAB-CSIC) using a Profilometer P16+ from KLA Tencor. In order to validate the results and provide further insight into the sample morphologies, atomic force microscopy (AFM) measurements were also carried out on two selected samples at ICMAB-CSIC with a MFP3D Asylum equipment, using Silicon tips (radius 9 ± 2 nm) mounted on levers with nominal stiffness constant $k = 2\ \mathrm{N\,m}^{-1}$ (AC240TS). Experimental details and measuring set-up can be found elsewhere [18] and AFM data were analysed using the WSxM free software [19].

Irradiated areas of the diamond samples were found to appear opaque after ion irradiation for all cases given in Table 1. Therefore, an optical micrograph clearly shows the irradiation pattern as generated by the mask used in each case, as shown in Fig. 1a. For this implantation, the selected mask allowed to irradiate $5.5 \times 5.5\ \mu\mathrm{m}^2$ squares, separated by 5.5 μm from each other in both perpendicular directions.

The resulting pattern was studied in detail by means of 2D profilometer scans on a selected set of samples. Irradiated (opaque)

Table 1
Experimental configurations for swift heavy ion irradiation of single-crystal diamond.

Ion species	Ion energy [MeV]	Ion fluence [10^{13} cm^{-2}]	Mask mesh / irradiated square side
Au	18.6	10	1 mm / 0.97 mm
Au	10.0	5	1 mm / 0.97 mm
Au	10.0	10	1 mm / 0.97 mm
Au	10.0	25	1 mm / 0.97 mm
Au	10.0	50	1 mm / 0.97 mm
Au	10.0	5	80 μm / 60 μm
Au	10.0	50	80 μm / 60 μm
Br	36.7	20	80 μm / 60 μm
Br	40.0	5	11 μm / 5.5 μm
Br	40.0	10	11 μm / 5.5 μm
Br	40.0	45	11 μm / 5.5 μm

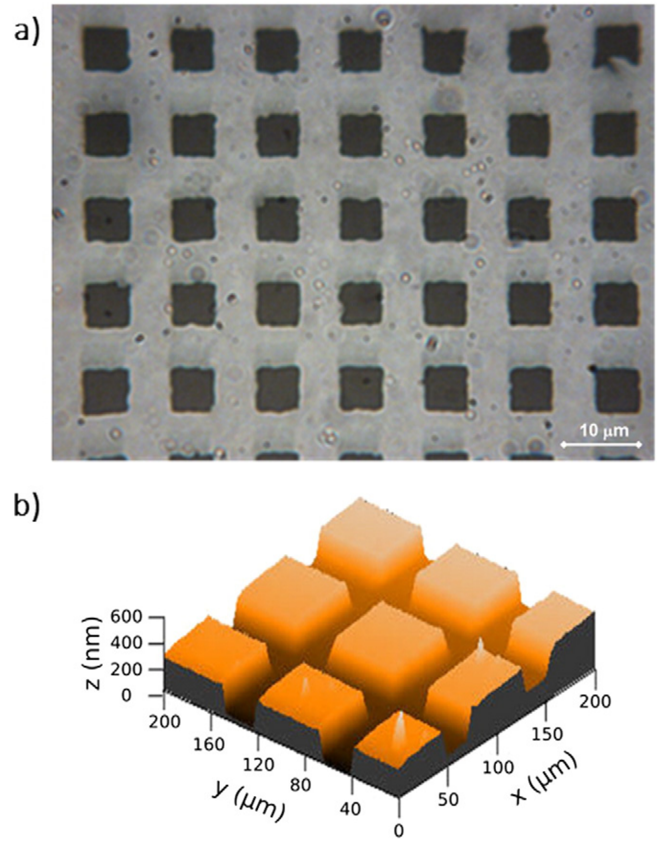

Fig. 1. a) Optical microscope image of a diamond sample after irradiation with a 40 MeV Br beam at a fluence of $5 \times 10^{13}\ \mathrm{cm}^{-2}$. An 11 μm mesh mask with 5.5 μm square apertures was used for irradiation. Dark areas of $5.5 \times 5.5\ \mu\mathrm{m}^2$ correspond to the irradiated sample surface, whereas the surrounding grey area corresponds to the unirradiated surface (i.e. the mask-covered regions). b) Surface topography, as measured with a profilometer, of a single-crystal diamond sample after irradiation with a 10 MeV Au beam at a fluence of $5 \times 10^{14}\ \mathrm{cm}^{-2}$. An 80 μm mesh mask with 60 μm square apertures was used for the irradiation.

regions have developed structural damage [10], generating buried volumes where the diamond lattice has been amorphized, leading to a density decrease and therefore a stress exerted on the surrounding crystalline diamond regions. The thin diamond slab on top of each of these modified volumes deforms and generates a swelling pattern on the surface, whereas unirradiated (transparent) areas do not deform. Irradiation using mesh masks gives rise to "landscapes" consisting of "plateaux" and "canyons", in which the latter have widths corresponding to the mask wire diameter, and a depth ranging from a few to hundreds of nanometers, depending on irradiation parameters. Fig. 1b shows an example, in which $60 \times 60\ \mu\mathrm{m}^2$ plateaux, ca. 200 nm in height, are surrounded by 20 μm wide canyons.

In order to crosscheck the height and sharpness of the plateau-to-canyon steps, as complementary to the profilometry measurements, two selected samples were measured by AFM in contact mode under controlled low load (≤150 nN). Since in the employed AFM set-up the accessible scanned areas are relatively small ($\leq 60 \times 60\ \mu\mathrm{m}^2$), a complete plateau could not be imaged. Therefore, the monitored areas were chosen to contain at least part of two neighbouring irradiated regions plus the intermediate unirradiated gap (Fig. 2a). With respect to standard profilometry, AFM is well known to give more accurate measurements of the step abruptness, with a negligible tip-convolution effect. Fig. 2b shows the 1D profile along the segment depicted in the 2D image (Fig. 2a). The measured height is 226 ± 5 nm, as can be observed in the magnified step edge profile (Fig. 2c). The sharpness of the generated features is ~2 μm. Additional information is obtained by measuring the root mean square (rms) surface roughness on both the surfaces