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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 irradiation is the thickening of the pre-existing graphitic layer. Cross-sectional SEM imaging was performed to directly measure the thickness of the modified layers, and subsequent selective etching of the buried layers was employed to both assess their graphitic nature and enhance the SEM imaging contrast. In particular, it was found that for optimal irradiation parameters the laser processing induces a six-fold increase the thickness of sub-superficial graphitic layers without inducing mechanical failures in the surrounding crystal. TEM microscopy and EELS spectroscopy allowed a detailed analysis of the internal structure of the laser-irradiated layers, highlighting the presence of different nano-graphitic and amorphous layers. The obtained results demonstrate the effectiveness and versatility of high-power laser irradiation for an accurate tuning of the geometrical and structural features of graphitic structures embedded in single-crystal diamond, and open new opportunities in diamond fabrication.

1. Introduction

Diamond is well known for its range of extreme mechanical, thermal and optical properties, which make it an attractive material for a variety of applications [1]. Nevertheless, diamond is a metastable allotropic form of carbon at standard pressure and temperature, and can be converted into graphite if an energy barrier is overcome [2]. Several approaches have been developed to induce this phase transition, among which ion-beam-induced graphitization [3–9] and laser-induced graphitization [10,11] play a prominent role. The former approach takes advantage of the ion-induced defect creation caused by nuclear collisions to amorphize the material and the subsequent thermal annealing to convert amorphized regions into a graphitic phase [3]. The latter approach is based on complex non-equilibrium dynamics induced by high-power light absorption, which were modelled with different theoretical approaches based on the non-radiative recombination of electron–hole pairs [11] or on a non-thermal ultrafast non-equilibrium

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phase transition [12,13].

Several previous studies explored the laser-induced graphitization process of single-crystal diamond: the first investigations dating back to the 80's were focused on realization of graphitic structures on diamond surface with direct writing or optical projection by means of excimer lasers [14], approached that was further investigated also in recent years [15]. Subsequently, new theoretical models of pulsed laser irradiation were proposed taking into account fast energy transfer mechanisms [16]. Consequently, in the last decade several works were carried out to exploit the possibility of realizing three-dimensional structures into diamond bulk by means of femtosecond [17,18] and picosecond [18–20] pulsed laser writing. Furthermore, the possibility of enhancing the resolution in the laser fabrication of the graphitic structures with the use of adaptive optical elements was recently demonstrated [21,22].

Direct laser-induced graphitization represents an extremely versatile technique with promising applications in different fields such as the realization of diamond-based particle detectors [23–27] and (upon the selective removal of the graphite) microfluidics devices for biomedical sensing [28].

On the other hand, this technique is limited by the poor geometrical quality of structures finishing, which is inherently caused by the nature of the graphitization process [18,20]. In order to overcome this limitation, laser-induced graphitization in diamond can be combined with a preliminary MeV-ion-induced graphitization stage. By taking advantage of the high degree of control on the geometrical properties (depth, thickness) of MeV-ion-induced buried graphitic structures in diamond allowed by the peculiar nuclear energy loss profile of MeV ions [29], this double-step procedure guarantees a better definition in the material micro-structuring [30] and also represents an interesting improvement in the realization of particle detectors [26,31,32], bolometers [33,34], bio-sensors [35–37], metallic-dielectric structures [38] and microfluidics [39].

In the present paper we report on the use of ns-pulsed laser irradiation for the structural modification and thickening of sub-superficial graphitic layers in diamond, which were realized by means of MeV ion implantation. The above-mentioned structures are imaged before and after the selective removal of the graphitic phase with respect to the surrounding diamond matrix, and are characterized in their structural properties by transmission electron microscopy.

2. Experimental

In the present study, a commercial synthetic (001) single-crystal diamond grown by High Pressure High Temperature method (HPHT) by ElementSix (Ascot, UK) was used. The diamond is $3 \times 3 \times 0.3$ mm^3 in size and it is classified as type Ib, having a nominal substitutional nitrogen concentration between 10 ppm and 100 ppm. The sample is cut along the 100 crystal direction and it is optically polished on the two opposite large faces.

The sample was implanted at room temperature at the "Service Faisceaux d'Ions" laboratory of the Nuclear Physics Institute (University of Claude Bernard Lyon 1) across one of the two main polished surfaces with a broad 2 MeV He^+ ion beam to deliver a uniform fluence of 1×10^{17} cm^{-2} across the irradiated area. During the implantation, the beam current was ~200 Na. The process of damage induced by MeV ions in matter occurs mainly at the end of ion range, where the cross section for nuclear collisions is strongly enhanced, after the ion energy is progressively reduced by electronic interactions occurring in the initial stages of the ion path [40]. Fig. 1 shows the strongly non-uniform depth profile of the density of induced vacancies ($\#_{vac}$ cm^{-3}) evaluated in a linear

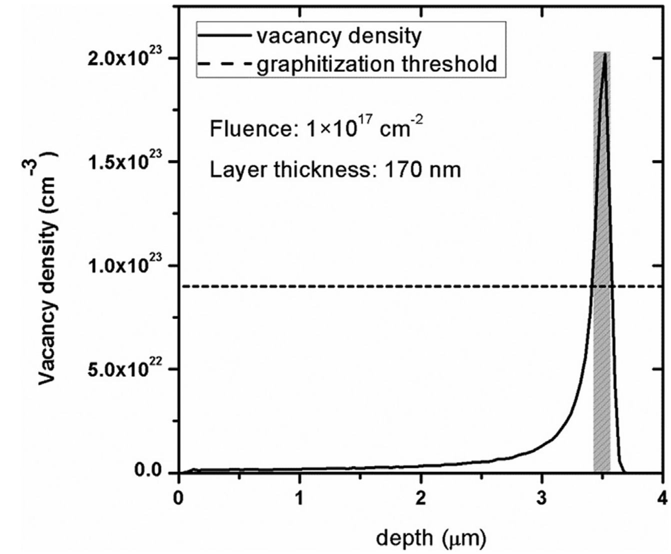

Fig. 1. Depth profile of the volumetric vacancy density induced in diamond by 2 MeV He^+ implanted at a fluence of 1×10^{17} cm^{-2}. The graphitization threshold is reported in dashed line. The amorphized region is highlighted by the grey area in correspondence of the intersection of the Bragg peak with the graphitization threshold.

approximation as the product between the implantation fluence ($\#_{ions}$ cm^{-2}) and the linear density of induced vacancies per single ion ($\#_{vac}$ cm^{-1} $\#_{ions}^{-1}$). The latter quantity was estimated with the "Stopping and Range of Ions in Matter" (SRIM)-2013.00 Monte Carlo code [29] in "Detailed calculation with full damage cascade" mode by taking an atom displacement energy value of 50 Ev [41]. The high density of damage induced by ion implantation promotes the conversion of the diamond lattice to an amorphous phase, which is located ~3.5 μm below the sample surface.

The above-mentioned implantation fluence allowed to overcome a critical damage density, usually referred as "graphitization threshold" [42], whose value in the above-mentioned linear approximation has been estimated as $\sim 9 \times 10^{2}2$ cm^{-3} for light MeV irradiation [43], as indicated in Fig. 1. Such a model of the damage profile has to be considered as a rough estimation since it results from a linearly cumulative effect of ion damage, i.e. by neglecting any damage saturation effects occurring at high damage levels such as self-annealing and vacancies interactions [44,45]. Nonetheless, in this context it can be considered as a satisfactory approach to estimate the depth and thickness of the buried region. After ion implantation, the sample was thermally annealed for 1 h at a temperature of 900 °C, which is suitable for the conversion of amorphous carbon to a graphitic phase, as confirmed by TEM studies [46–48]. Concurrently, the annealing process restores the pristine diamond structure in the lightly-damaged cap layer, i.e. the region comprised between the surface and the buried graphitic layer [49,50]. The process was carried out in vacuum ($p \approx 10^{-6}$ mbar) to avoid accidental etching of the diamond surface due to oxidation.

The ion-implanted side of the sample was subsequently irradiated with nanosecond-pulsed Nd:YAG laser (EzLaze3 by New Wave) equipped with a Q-switching system. This laser source generates pulses of 4 ns duration with a repetition rate of either 1 Hz or 5 Hz. Two different emission wavelengths can be selected, i.e. 1064 nm and 532 nm, the second one being obtained by means of an angle-tuned KTP crystal. The laser beam is focused onto the sample with a microscope supplied with 5×, 20× and 100×objective lenses. The co-axial imaging through the microscope offers the opportunity of monitoring the sample processing