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Micro-Raman spectroscopy of near-surface damage in diamond irradiated with 9-MeV boron ions

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A B S T R A C T

We have studied the near-surface damage in a diamond crystal caused by irradiation with swift boron ions and its healing after high-temperature annealing. A diamond crystal was irradiated with 9-MeV $^{11}B^{3+}$ ions with fluence values between 1×10^{15} and 4.42×10^{16} ions/cm^2 to generate various levels of lattice damage. The ions loose energy to the lattice and, according to simulations, stop at a depth of about 5 µm, where they form a thin buried implantation layer. For the near-surface layers damage is produced by the ions at high kinetic energy before they slow down. Only intrinsic defects can be produced, with no boron atoms. The lattice damage of the near-surface layers and its recovery after annealing for 1 h at 1000°C were studied by Raman and photoluminescence spectroscopies. Back-scattered light from a 514.5-nm laser beam was collected from the sample surface, probing a depth of a few micrometers. We observe some disordering of the lattice plus the formation of neutral vacancies, interstitial and other lattice defects. After annealing the Raman spectrum shows a significant recovery of the lattice order and the disappearance of isolated neutral vacancies. Residual damage is confirmed by the luminescence spectrum, that shows the appearance of new spectral features.

1. Introduction

Diamond is a material with extraordinary technological potential due to its exceptional physical and chemical characteristics, such as outstanding hardness, excellent thermal conductivity, and high Debye temperature. Doping with impurities can add new optical and electrical properties. For example, color centers associated with dopants can increase the emission efficiency of an indirect-gap material like diamond [1]. Boron doping is particularly interesting. Although diamond is an electrical insulator, concentrations of boron ions ($n \approx 10^{17}$–10^{19} cm^{-3}), acting as charge acceptors, turn diamond into a *p*-type semiconductor. This enables its use for microelectronic and photonic [2] devices. Moreover, in 2004, Ekimov et al. [3] found superconductivity at $T_c \approx 4$ K in heavily boron-doped diamond, synthesized using high-pressure/high-temperature methods. Several other groups confirmed this finding by growing superconducting boron-doped diamond crystallites by chemical vapor deposition (CVD) [4].

Because of the short and strong C–C bonds, incorporation of dopants into the diamond lattice can be very difficult under thermal equilibrium. Therefore ion implantation is an interesting alternative for diamond doping [5]. Focused ion-beam irradiation, in particular, enables selective doping in a well-controlled way. The implantation of high energy ions in the MeV range allows for the fabrication of buried doped layers and also graphite electrodes [6–8]. Graphitization has been reported to occur after high temperature annealing for irradiations where the lattice damage is above a threshold of 10^{22} vacancies/cm^3 [9]. Nonetheless, when the implantation layer is buried, graphitization seems to be prevented in part by the large internal pressure in the surrounding bulk crystal [10–12] and, additionally, by high temperature implantation [8]. In that way damage thresholds close to 10^{23} vacancies/cm^3 have been reached [10,12].

In this work, we study the damage in the diamond lattice caused by boron ion irradiation and its healing after high temperature annealing, with ion energies as high as 9-MeV and fluences up to

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4.42×10^{16} ions/cm^3. We have used Raman and photoluminescence spectroscopy, which are very sensitive to the lattice damage and quite complementary [8,10-15]. We focus specifically on the damage of the near-surface layers, well separated from the deep boron implantation layer. In these cap layers, boron ions are absent and damage is produced by the ions before they slow down, at high speed in an energy range that has not been well studied before, except for very light atoms like H or He.

2. Material and methods

Boron implantations were conducted at the microbeam line of the Center for Micro Analysis of Materials (CMAM) in Madrid, using a focused ion beam with a size of about $5 \times 3\ \mu m^2$ and a beam current ≈500 pA, following the procedure previously described [16]. The target was a high-purity (*Electronic Grade*) type IIa single-crystalline diamond plate grown by CVD techniques by Element Six [17]. Concentrations of nitrogen and boron impurities are reported to be well below 5 ppb and 1 ppb, respectively. A (001) face of the diamond crystal was irradiated with a focused ion beam of 9 MeV $^{11}B^{3+}$ ions with fluence values up to 4.42×10^{16} ions/cm^2, as detailed in Table 1. Irradiations were conducted in each case along parallel stripes with typical areas of 25 μm× 500 μm.

Aiming to reduce the damage, the sample was later annealed in a furnace for 1 h at 1000°C. To avoid possible thermal stresses, heating and cooling ramps were performed from room temperature to 1000°C and back, each lasting 3 h. The sample was put in a clean alumina crucible and inserted into a vacuum-sealed quartz ampoule, with a low-pressure (100 mbar) of pure helium inside as thermal exchange gas.

A simulation carried out with the SRIM code [18] shows (see Fig. 1) that 9 MeV boron ions penetrate into diamond and loose kinetic energy to the lattice until they are finally stopped at a depth of about 5.0 μ m (Fig. 1 (b)). At this depth a thin boron implantation layer or stopping layer is formed. The calculated density of vacancies (including ion recoil effects) as a function of depth also shows a maximum at about 5.0 μ m (Fig. 1 (a)). The obtained peak values are 3.31×10^{23} vacancies/cm^3 and 3.16×10^{21} atoms/cm^3, respectively, for the damage and the boron concentration at the highest fluence. The nuclear and electronic stopping powers are 1.59×10^{-3} and 1.75 keV/nm, respectively. Under these conditions nearly all damage is caused by the nuclear stopping power [19].

Irradiation damage above a certain threshold produces amorphization of the crystal lattice [9]. Later high temperature annealing can lead to crystallization into graphite instead of diamond structure. Thus a graphitization threshold of 10^{22} vacancies/cm^3 has been reported for implantation with keV ions [9], which is represented in Fig. 1 by a horizontal dashed line. We have studied the layers near the surface where there is no boron doping. Also, no graphitization is expected for these layers because their damage level is well below the threshold. All irradiated stripes exhibited a marked darkening. After annealing, only the stripes with larger fluences remained dark, the others recovering transparency. However, by mere optical inspection of the samples, we are not able to discern whether the remaining dark color of higher fluence stripes is due to graphitization of the end-of-range layer or rather to the residual, unhealed damage.

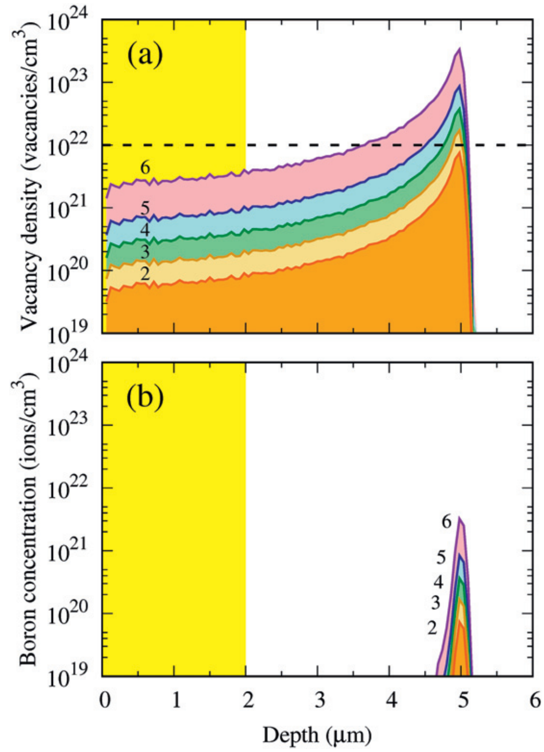

Fig. 1. SRIM simulations for 9 MeV boron ions implanted on a diamond sample. (a) Density of vacancies versus depth. (b) Concentration of implanted boron ions (9 MeV) versus depth. The fluence values for each curve are (2) 0.1×10^{16}, (3) 0.23×10^{16}, (4) 0.5×10^{16}, (5) 1.15×10^{16}, and (6) 4.42×10^{16} ions/cm^2. The horizontal dashed line shows the reported graphitization threshold [9] . The shaded area on the left side marks the estimated probing depth by Raman and photoluminescence experiments.

Raman spectra of the boron irradiated stripes were measured at room temperature before and after annealing with a Renishaw Ramascope 2000 spectrometer. The 514.5 nm wavelength from an argon ion laser was used for excitation. The laser beam went through a spatial filter to get a Gaussian intensity profile. Light was focused on the sample surface with a 100× microscope objective having a numerical aperture of N.A. = 0.95. The spectrometer was configured in quasi-confocal mode. The depth of the volume probed by the Raman spectrometer is approximately 2 μm in air due to light diffraction [20]. When focusing inside the diamond sample it expands significantly because of spherical aberrations produced by the refraction at the air–sample interface [21]. To minimize these aberrations the focus was always kept at the sample surface, so that only one half of the probing volume gets inside the sample. In this case, the sample depth probed by the experiments is determined mainly by diffraction [22], and we estimate it to be not larger than 2 μm, as indicated in Fig. 1. No signal is expected from the stopping layer with the boron implanted ions nor from the unaltered diamond lattice underneath.

Table 1
Density of vacancies (including ion recoil effects) and boron concentration produced by irradiation of diamond with 9-MeV boron ions as a function of ion irradiation fluence, calculated using SRIM simulations (see Fig. 1). The density of vacancies is given at the sample surface and at the maximum of the damage layer 5 μm deep. The concentration of boron ions is at the center of the implantation layer at a depth of about 5 μm.

No.	Fluence (10^{16} ions/cm^2)	Vacancies (@ surface) (10^{21} cm^{-3})	Vacancies (@ max.) (10^{21} cm^{-3})	Boron atoms (@ max.) (10^{21} cm^{-3})
1	0	0	0	0
2	0.10	0.04	7.5	0.07
3	0.23	0.10	17	0.17
4	0.50	0.23	37	0.38
5	1.15	0.52	86	0.85
6	4.42	2.01	331	3.16