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Surface Modification of Polycrystalline Diamond Compacts by Carbon Ion Irradiation

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Abstract

Selective modification (e.g. defect creation and amorphization) of diamond surfaces is of interests for functional diamond-based semiconductors and devices. Bombarding the diamond surface with high energy radiation sources such as electron, proton, and neutrons, however, often result in detrimental defects in deep bulk regions under the diamond surface. In this study, we utilized high energy carbon ions of 3 MeV to bombard the polycrystalline diamond compact (PDC) specimen. The resultant microstructure of PDCs was investigated using micro Raman spectroscopy. The results show that the carbon bombardment successfully created point defects and amorphization in a shallow region of ~500 nm deep on the diamond surface. The new method has great potential to allow diamond-based semiconductor devices to be used in numerous applications.

Keywords: Selective modification, diamond-based semiconductors, polycrystalline diamond compact, Ion Irradiation

1 Introduction

Diamond is the hardest known material with a high atomic density and strong inter atomic bonds (covalent bond) between carbon atoms. It has excellent mechanical, optical and thermal properties for applications in machining tools, plastic processing tools, and anti-abrasion element etc. (Tanabe, 2007). Small concentration of point defects can drastically modify the properties of diamond such as optical and electrical for various applications (Field 1992, Crawford 1975, Gupta 2010, Campbell 2000).

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Residual defects in diamonds cause charge carrier trapping and compensation which degrades the electrical properties of diamond based electronic devices such as radiation detectors (Prawer 2004). The creation of photoluminescence centers such as the vacancy sites in diamond has promising applications in the development of optical solid state quantum devices (Ager 1994, Collins 1982, Martin 1999, Martin 1999, Sonnefraud 2008, Waldermann 2007, Wang 2005).

Irradiation of a substance by energetic particles can create lattice defects, such as interstitial and vacancy defects. Vacancies may also aggregate leading to larger dislocations (Field 1992, Seo, 2011). High energy particles such as electrons, neutrons, and protons are often used for irradiation treatment of materials (Campbell 2000, Newton 2002, Campbell 2002, Grilj 2013, Lohstroh 2008, Lohstroh 2010). However, these high energy radiations often result in defects in the deep bulk region as the projection range of these particles is quite high (Campbell 2000, Grilj 2013, Lohstroh 2008, Lohstroh 2010). The deep defects can be detrimental to the functioning of semiconductor based electronic devices (Campbell 2000, Ager 1994, Campbell 2002, Jamieson 1993, Prawer 1995).

In this paper we report a new method to create point defects in polycrystalline diamond compact (PDCs) using carbon ion bombardment. The host carbon atom at the lattice site is displaced when it attains an energy known as displacement energy E_d upon collision with carbon ion or by other carbon atoms. Sufficient energy has to be transferred to the carbon atom so that it does not recombine immediately, i.e. enough energy for it to move away from its original lattice site. E_d has been shown to be in a wide range from 25 – 80 eV (Campbell 2002), which corresponds to a striking particle energy, in the range 165 - 197 KeV (Campbell 2002). Most of the lattice damage is created not by the bombarded particles but by the impact of primary knock out atoms (Campbell 2000, Campbell 2002, Prawer 1995). The large carbon ions allow a low projected range so that defects are only created in and near a shallow surface region on diamond. Surface amorphization modifies the surface electrical properties of the diamond to be utilized as electrical interconnects. The vacancy and interstitial atoms on diamond surfaces stays immobile (Campbell 2002, Grilj 2013) until subjected to a temperature greater than 550 ºC. A selective irradiation of surfaces can lead to significant applications of diamond semiconductors for temperature below 550 ºC.

2 Experimental

2.1 Irradiation of PDC specimens

Polycrystalline diamond compact (PDC) samples (~8 mm in diameter and 5 mm in thickness) were irradiated at the Characterization Lab for Irradiated Materials (CLIM) using a National Electrostatics Corporation (NEC) 1.7 MV Pelletron accelerator at University of Wisconsin-Madison. The schematic of the equipment is shown in Figure 1 (Field 2013). The PDC sample pairs, as shown in Figure 2, were cemented onto stainless steel sample holders using a water-soluble silver paste from Ted Pella. The irradiation chamber was vacuumed to a pressure of ~1×10^{-6} Torr before and during the irradiation, with samples exchanged between each irradiation cycle. Negative carbon ions were produced via Cesium sputtering (SNICS) of graphite target and converted to positive ions using a nitrogen stripping gas. These C^{2+} ions were accelerated to a total energy of 3.0 MeV, and steered onto the samples. The incident ion beam, normal to the sample face, was rastered across a well-defined aperture with area of 1.874 cm^2 exposing the samples uniformly to the C^{2+} ions. The beam current ranged from 2 - 4 μA for an ion flux of 6.7×10^{12} to 1.4×10^{13} ion/cm^2s, based on the aperture size. The sample temperature was recorded on the right and left sides of the sample holder using two type-K thermocouples. Cool air spray was used to maintain the sample temperature during the irradiation process.

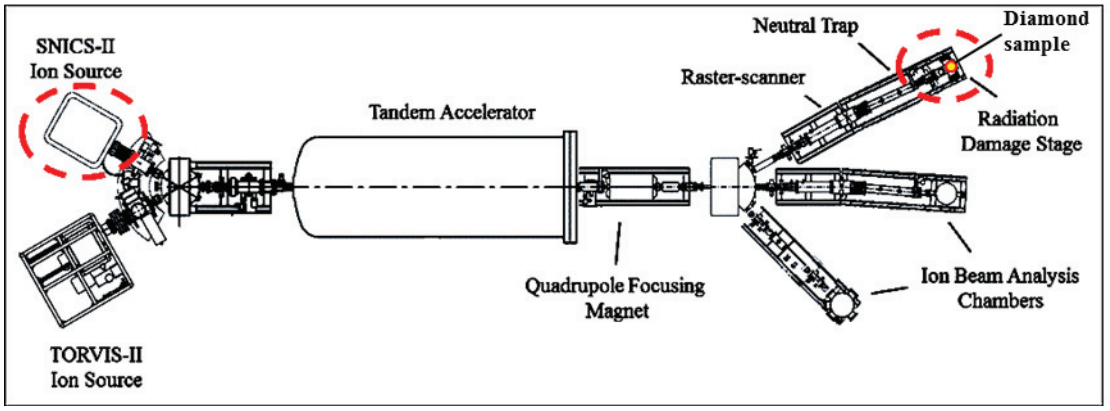


Figure 1: Ion Beam Laboratory beam line schematic at University of Wisconsin (Field 2013)

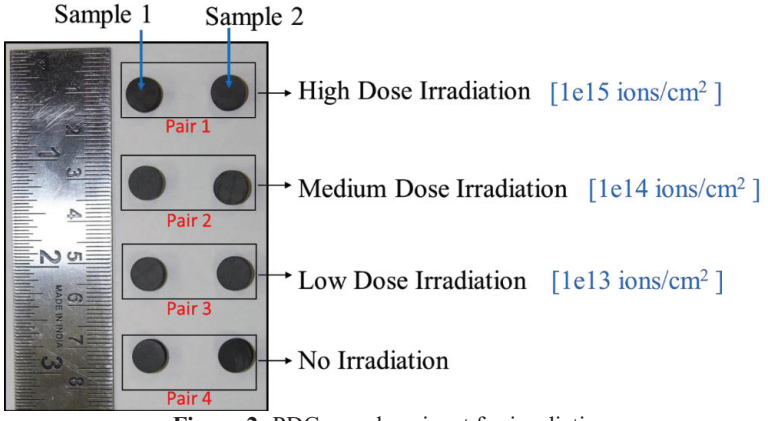


Figure 2: PDC sample pair set for irradiation

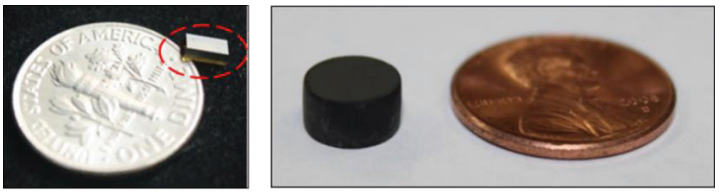
Three pairs of PDC samples were irradiated with different dosage levels while the ion energy (~3 MeV) remained constant. Pair 1, was irradiated at a high dosage level (5×10^{15} ions/cm^2); pair 2, was irradiated at a medium dosage level (5×10^{14} ions/cm^2) and the pair 3, irradiated at a low dosage level (5×10^{13} ions/cm^2). Table 1 presents other parameters used during the irradiation of PDC samples.

Irradiation	Desired Fluence (ions/cm^2)	Achieved Fluence (ions/cm^2)	Average Temperature (°C)	Average Current (µA)	Time (s)
Low	5×10^{13}	5.765×10^{13}	16.91	4.3	4
Medium	5×10^{14}	5.665×10^{14}	51.6	3.277	57
High	5×10^{15}	5.002×10^{15}	118.4	1.67	857

Table 1: PDC irradiation parameter

2.2 Diamond surface analysis using Raman spectroscopy

Single Crystal Diamonds (SCD) and Polycrystalline Diamond Compacts (PDC) surfaces, as shown in Figure 3, were analyzed using Micro Raman Spectroscopy (LabRAM ARAMIS) to analyze carbon structural phase and bonding configuration i.e. to quantify the diamond to graphite ratio or sp^3 /sp^2 carbon bond ratio. Raman spectroscopy is a widely used characterization technique for a variety of carbon based materials due to its ease of use, noninvasiveness and characteristic sharp vibrational bonds (Gupta 2010, Gupta 2009).



(a) (b)

Figure 3: (a) SCD used in turning tools, (b) PDC used for deep drilling tools

The micro Raman spectra for assessing the lattice structure and probing the carbon bonding configuration was recorded by a 532 nm wavelength laser, using Labram Aramis by Horiba. The objective lens of 50X magnification was used for all measurements. The induced power was nearly 10 kW/cm^2. The exposure time was set to 3 sec, acquisition time was set to be 10 sec and 20 accumulations were taken to average each spectrum. All the Raman spectra readings were fitted using Fityk software (version 0.9.8) based on Levenberg-Marquardt method.

3 Results

The C^{2+} ion bombardment corresponding to a projection range of R_p = 1.6 µm, as shown in Figure 4, was carried out with fluences of 5.7×10^{13}, 5.8×10^{14}, and 5×10^{15} C/cm^2, which correspond to damage levels of 2.7×10^{-4}, 2.6×10^{-3}, and 2.3×10^{-2} dpa, i.e., displacement per atom, at the depth of 0.5 µm (Figure 4), respectively. The maximum concentration of irradiated carbon is 0.29 at. % at the fluence of 5×10^{15} C/cm^2 which do not disturb the sample chemistry. The damage levels in the units of dpa were calculated according to Eq. (1):

$$damage\ level = \frac{\nu \cdot \phi}{N_0} \tag{1}$$

The number of displacements ν $\left[\frac{10^8 vacancy}{ion \cdot cm^2}\right]$ were taken from a TRIM calculation (SRIM 2008.03, "full cascade option" (Ziegler 2013)) assuming the displacement threshold energy to be E_d = 25 eV. Φ [ion/cm^2] denotes the ion fluence taken from the experiment and N_0 [at/cm^3] the atomic density of diamond which is 1.77×10^{23} cm^{-3}. Subsequent to displacement, the defects produced in the collision cascade, diffuse and annihilate. These effects were not included in the program as the damage structure will be far more complex than the calculated one.

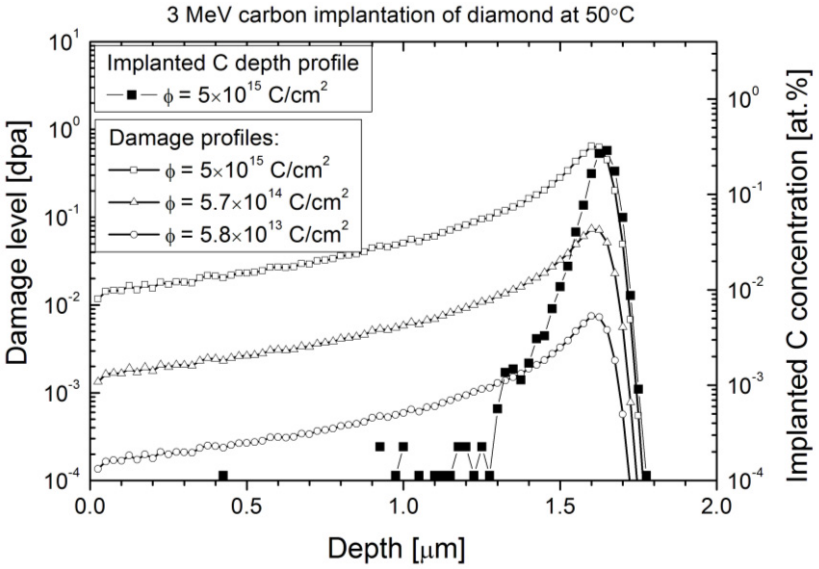


Figure 4: Damage distribution and the depth profile of implanted carbon in diamond irradiated with 3.0 MeV $C2^+$ ions to damage levels of 0.04, 0.4, and 1.2 dpa

Each pair of PDC samples were analyzed before and after irradiation using Raman spectroscopy, as shown in Figure 5 (high, medium, and low dosages from top to bottom sequentially). The irradiation of the specimens with carbon ions has tremendous influence on the crystal properties of diamonds. The sample pairs irradiated at high dosage levels resulted in significant amount of amorphization. This onset of amorphization is noticeable by the broadening of sp^3 and sp^2 peaks as well as by the overlap of the sp^3 and sp^2 peaks. The amorphization effect is weakened at medium dosage levels and the effect is still lowerfor low irradiation dose. As the amorphization of a crystalline material is directly related to the number of defects in the material, it can then be said that the high level irradiation of PDCs resulted in creation of higher amount of point defects followed by mid-level and low level irradiation.

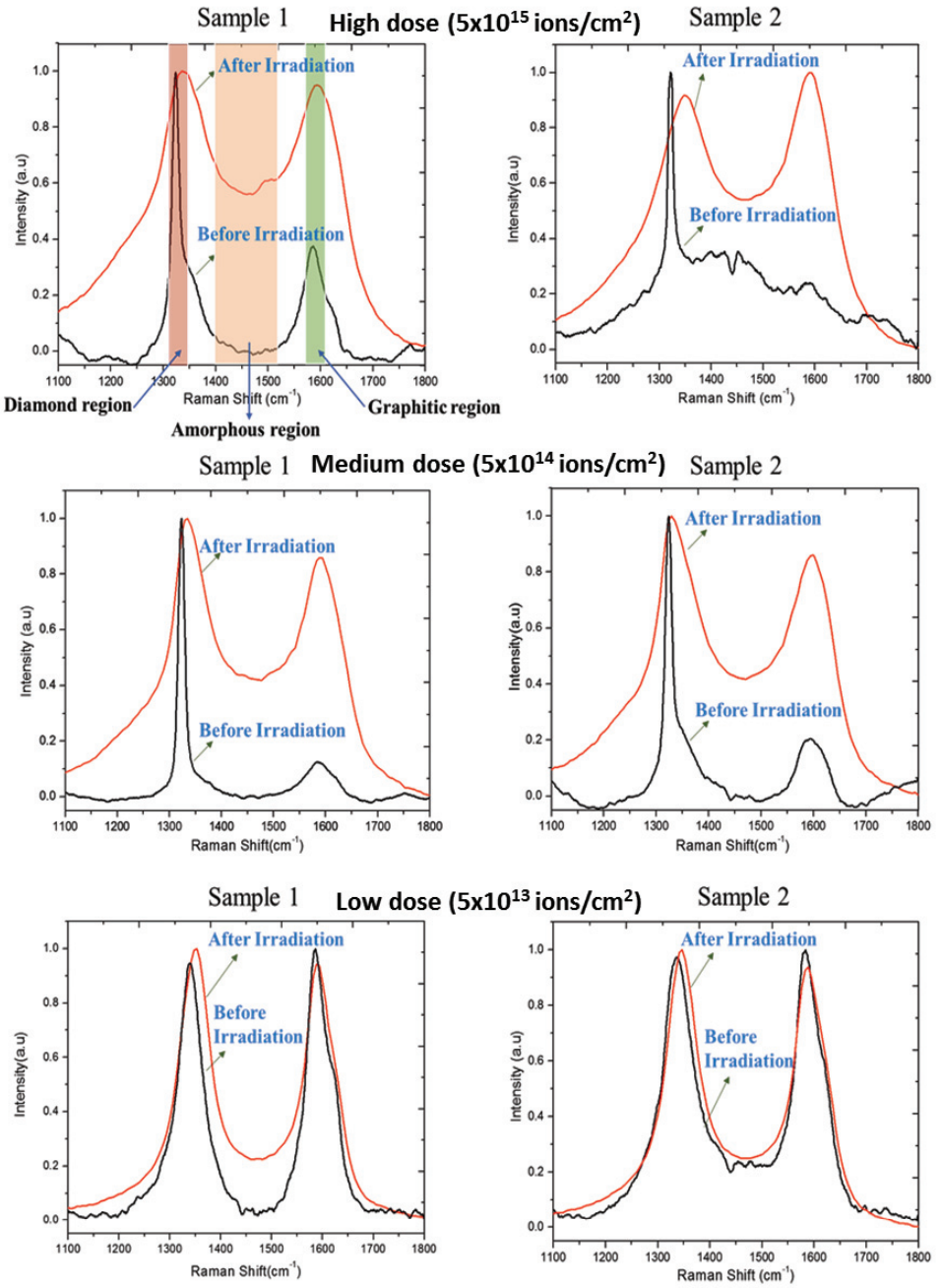


Figure 5: Raman spectroscopy of PDC sample pairs after ion irradiation (High, medium, and low dosages from top to bottom consequentially)

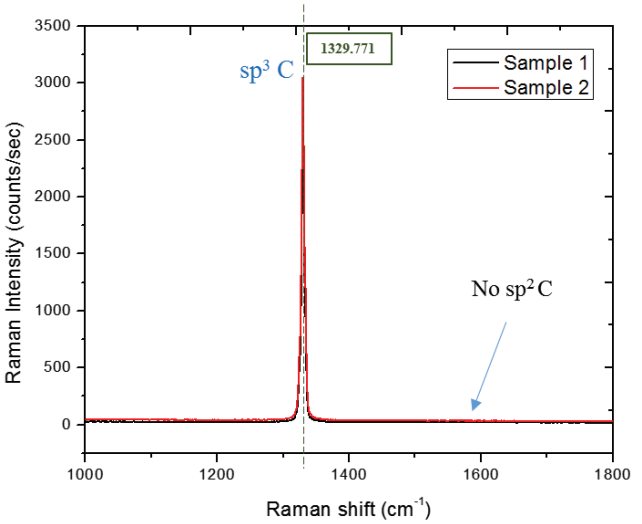


Figure 6: Micro-Raman spectra of SCD indicating diamond characteristic peak at ~1330cm-1 and no graphite phase

The Raman spectral analysis of SCD as shown in Figure 6 revealed the zone center phonon peak at ~1330 cm^{-1} and between 1550 - 1600 cm^{-1} which are characteristics peaks for diamond (sp^3 Carbon) and graphite (sp^2 Carbon) respectively. The spectral characteristic peaks are nearly consistent for all the samples. The sp^3 carbon quantity is evaluated by integrating the area under the diamond peak to that of the rest of the spectrum between 1100 and 1800 cm^{-1} with a resolution of 0.76 cm^{-1}. In the present study, we found that the sp^3 to sp^2 ratio in the SCD is nearly 100 % as evident from Figure 6. The sp^3 to sp^2 ratio varies between 50 - 70 % for PDC samples as indicated in Figure 5. The spectrum of PDC samples even show broader peaks caused by phonon scattering indicating the presence of impurities and defects.

A comparative analysis of all the samples irradiated at different levels of irradiation is also presented in Figure 7, which clearly signifies that the amount of dosage levels is truly related to the amount of amorphization thereby the number of point defects.

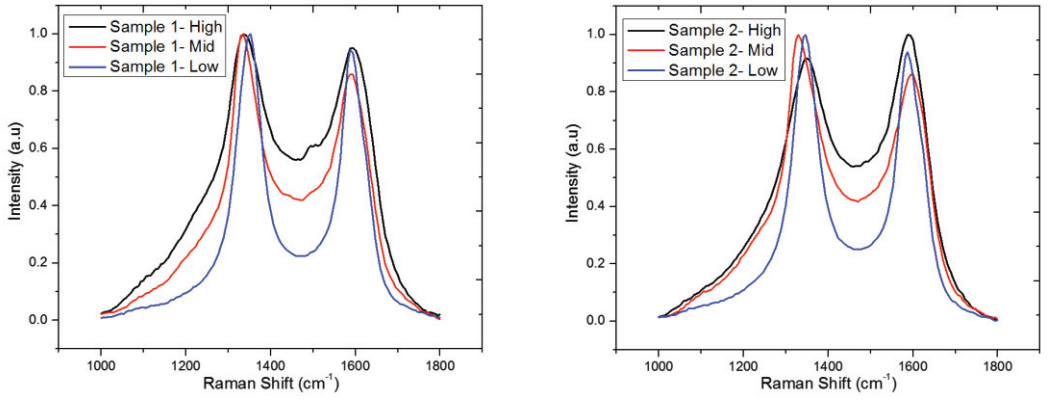


Figure 7: Comparison of PDC samples irradiated at High, Medium and Low dosage levels

Hence, it can be stated that the irradiation of PDCs with carbon ions results in significant amount of point defect creation. Moreover, since the irradiation source is carbon the PDC specimens do not undergo contamination. This helps the diamond surface to maintain its characteristic properties.

The results from this study were compared with studies done by other researchers (Newton, 2002, Grilj 2013, Lohstroh 2008, Bruzzi 2001) who used various particles to damage diamond (see Table 2). To find correlation between studies performed at various energies, fluxes, and fluence, all the data was normalized against dpa which is better than fluence to represent the effect of irradiation on material properties. SRIM (Ziegler 2013) was used to calculate the projected range and the damaged level in diamond implanted by protons.

Paper	Particle	Implantation Energy	Projected Range	Implanted Fluence [Particle/cm^2]	dpa	Temp. [K]
(Grilj 2013)	Protons	4.5 MeV	96 µm	1.7×10^{12}	2×10^{-8} dpa at 10 µm	-
(Lohstroh 2008)	Protons	2.6 MeV	38 µm	5×10^{15}	5.6×10^{-5} dpa at 10 µm	-
(Bruzzi 2001)	Neutrons	1 MeV	13 cm	2×10^{15}	8.2×10^{-6} dpa	-
(Newton 2002)	Electrons	2 MeV	1.7 cm	7×10^{17}	2.7×10^{-5} dpa	-
This Study	Carbon ions	3 MeV	1.6 µm	5.8×10^{13} 5.7×10^{14} 5×10^{15}	2.7×10^{-4} dpa at 0.5 µm 2.6×10^{-3} dpa at 0.5 µm 2.3×10^{-2} dpa at 0.5 µm	325 391 390

Table 2: Defect creation by various high energy particles

The range of neutrons was estimated by using the most basic definition of range:

$$R = \frac{E_0}{\frac{dE}{dx}} \tag{2}$$

Where E_0 is the incident energy, here taken as 1 MeV for fast neutrons, and dE/dx is the stopping cross-section which for neutrons can be expressed as follows:

$$\frac{dE}{dx} = \bar{T} N_0 \sigma_s = \frac{2M}{(1+M)^2} E_0 N_0 \sigma_s \tag{3}$$

Where M = 12 [u] is the atomic mass of carbon and $\sigma_s = 3$ [b] is the total cross-section taken from the ENDF-VII database (http://atom.kaeri.re.kr/). The projected range of electron was taken from the ESTAR database (*ESTAR program)*. The damage level in neutron irradiated diamond was calculated using the following equation from (G. S. Was, 2007):

$$R = N_0 \sigma_s \phi \frac{2ME_0}{4E_d(1+M)^2} \tag{4}$$

Where implanted fluence ϕ was taken from Table 2 and the remaining symbols are explained in the text above. Lastly, the damage caused by electrons was calculated by combing the displacement rate equation (G. S. Was, 2007) with the interaction cross-section from (http://atom.kaeri.re.kr/). Significant amount of point defects could be easily created at the shallow regions of PDCs (~500 nm) as compared with the results obtained by various other high energy particles as shown in Table 2, where the defects creation was possible only into the deeper bulk of the PDCs.

4 Conclusion

High energy carbon ions were utilized to create point defects in the PDCs. PDC specimen were bombarded by carbon ions of 3 MeV at three different fluences, i.e. at 5×10^{15} ions/cm^2 , 5×10^{14} ions/cm^2 , 5×10^{13} ions/cm^2 respectively. Although a maximum defect depth reached ~1.6um, significant number of point defects were successfully formed at a shallow surface region of about 500 nm under the surface. This is quite significant when compared to other defect counts as mentioned in Table.2.The resultant amorphization of PDCs was validated by micro Raman spectroscopy. This experiment successfully determines the required dose, energy, fluence of carbon ions that is adequate to create point defects at the shallow surface region. This approach of inducing defects on surface with carbon ions also has the advantage of the overall chemistry of the diamond surface and bulk remaining the same. The new method has great potential to allow diamond-based semiconductor devices to be used in numerous applications.

5 Acknowledgement

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