Diamond & Related Materials 49 (2014) 1–8

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Electron microscopy profiling of ion implantation damage in diamond: Dependence on fluence and annealing☆

E.K. Nshingabigwi [a,b,*], T.E. Derry [a], S.R. Naidoo [a], J.H. Neethling [c], E.J. Olivier [c], J.H. O'Connell [c], C.M. Levitt [a]

[a] *DST-NRF Centre of Excellence in Strong Materials and School of Physics, University of the Witwatersrand P. O. WITS, 2050, Johannesburg, South Africa*
[b] *Department of Physics, University of Rwanda/Huye Campus, P.O. Box 117, Huye, Rwanda*
[c] *Centre for HRTEM, Nelson Mandela Metropolitan University, 6031, Port Elizabeth, South Africa*

A R T I C L E   I N F O

Available online 1 August 2014

Keywords:
Diamond crystal
High resolution transmission electron microscopy
Cross-sectional TEM
Implantation
Radiation induced effects

A B S T R A C T

The doping of diamond by ion implantation has been feasible for 25 years, but with the proviso that low dose implants can be annealed whereas high dose implants "graphitize". An understanding of the types of defects, and their depth profiles, produced during the doping/implantation of diamond remains essential for the optimization of high-temperature, high-power electronic applications. This study focuses on investigating the nature of the radiation damage produced during the implantation of carbon ions into synthetic type Ib and natural diamonds using a spread of 4 energies, corresponding to typical doping energies, according to the CIRA (Cold-Implantation-Rapid-Annealing) routine, as well as a single energy implantation at room temperature. Both conventional and high resolution cross-sectional electron microscopies were achieved and used to analyze the implanted diamonds in conjunction with electron energy loss spectroscopy (EELS) and selected area diffraction (SAD). The cross sections were obtained using two different preparation methods.

For low fluence implantations, using the CIRA routine, it is confirmed that the damaged diamond regains its crystallinity after annealing at 1600 K. However, above the amorphization threshold fluence, followed by rapid annealing at 1600 K, the whole implanted layer consisted of primarily amorphous carbon. High resolution TEM shows that the implanted layer consists of nano-regions with bent (002) graphitic planes and regions of amorphous carbon. The interface between the implanted layer and the diamond substrate near end of range shows diamond nanocrystallites, interspersed between regions of amorphous carbon and with bent (002) graphitic planes. There is no evidence for epitaxial regrowth. For high dose single energy ion implantation at room temperature, the unannealed layer shows a high degree of disorder at the maximum ion range, with some alignment of basal planes related to graphitic carbon, but with some of the diamond structure still partially intact. The implanted range included a diamond layer above the damaged region. This diamond layer showed no evidence of amorphous carbon.

1. Introduction

The doping of diamond by ion implantation is a promising technique for the fabrication of diamond-based electronic devices [1,2] using a spread of ~100 keV ion energies and the CIRA (Cold-Implantation-Rapid-Annealing) technique [1]. In this method, implantation of e.g. B^+ ions, with a possible pre-implantation of C^+, is carried out at liquid nitrogen temperature to freeze in a dense "soup" of vacancies and interstitials. A very rapid anneal to well above the defect mobility temperature (say 1600 K) leads to a high probability of dopant atom capture into a vacancy, i.e. activation.

However, previous studies have indicated that above a critical dose of about 5.2×10^{15} carbon ions per cm^2, the implanted diamond layer retains extensive damage and the diamond structure is partially destroyed [3]. Below the critical dose, the implantation damage in diamond anneals out and the diamond structure is recovered [4]. Similarly, Kalish et al. [5] have studied the nature of damage in ion-implanted and annealed diamond using Raman spectroscopy and reported that below the critical fluence, the damaged diamond anneals back to diamond, while above the critical threshold, an amorphized layer of sp^2 bonded carbon is formed. It is clearly important to visualize the different types of defects involved, and their depth profiles, to replace speculation over the last 25 years.

No direct observations of the damage depth profiles using cross-sectional transmission electron microscopy (X-TEM) of 10–100 keV dopant ion damage in annealed diamond have, apparently, been attempted due to the difficulty of thin specimen preparation, before the availability of focused ion beam milling (FIB), but a method was

---

☆ Presented at the International Conference on Diamond and Carbon Materials (DCM 2013), September 2–5, 2013, Riva del Garda, Italy.

* Corresponding author at: University of Rwanda/Huye Campus, P.O. Box: 56 Huye Rwanda, University Avenue, Rwanda. Tel.: +250 787900144 (mobile).
E-mail addresses: e.nshingabigwi@ur.ac.rw, enshingabigwi@yahoo.fr (E.K. Nshingabigwi).

http://dx.doi.org/10.1016/j.diamond.2014.07.010
0925-9635/

developed and reported in [4] together with some preliminary results. Recent studies involving the direct examination of defects in irradiated and annealed diamond by transmission electron microscopy [6] using MeV energies and Si ions, have also reported that diamond transforms to amorphous carbon when a critical threshold is surpassed. The amorphous carbon transforms to a moderately crystalline graphitic region upon annealing for 24 h at 1350 °C. However, that work is not cognate to 100 keV doping with lighter ions.

This paper presents some of the first comprehensive cross-sectional results of conventional microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) and an electron energy loss spectroscopy (EELS) investigation of the damaged layer in diamond implanted with carbon self-ions (to avoid chemical effects) using a low and a high fluence which are below and above the critical dose defined above, respectively. Both mechanical and FIB sample preparation techniques were used, enabling an assessment of any additional damage or precipitates introduced by the Ga^+ beam used in the latter case.

2. Experimental details

In our initial study on ion implanted diamond there were few FIB facilities. In order to circumvent this we developed a technique that would allow us to prepare the implanted diamonds for X-TEM studies, as elaborated in [4]. Slicing of implanted bars to the 40 μm thickness required for conventional ion-beam thinning to electron transparency is not available for diamond. Accordingly, slices of ~500 μm thick were cut from single crystal natural type Ia and synthetic diamond type Ib with {110} orientation and plane polished down to ~40 μm using a specially stabilized scaife. It is important to realize that the temperature during polishing can rise to 800 °C or more, and it must not be done after temperature-controlled implantation and/or annealing. In order to prepare the cross-sections, the slices of about 40 μm were then implanted edge-on, at liquid nitrogen temperature, followed by rapid thermal annealing for 30 min, at 1600 K, in an argon atmosphere. The implantation geometry is illustrated in Fig. 1 which is taken from [4]. Note that the very small sample width is not a problem because the implant depth is two orders of magnitude less.

The implantation was carried out at iThemba LABS (Gauteng), South Africa, using the Varian 200-20A2F ion implanter. The diamond samples for CIRA processing were C^+-implanted using ion energies and fluences shown in Table 1 and they were tilted about 7° to the incident beam direction so as to minimize the effects of channeling. The critical angles for a <110> axis are 3.3° for 150 keV and 5.7° for 50 keV, so this is sufficient. A scanned beam at a rate of ~10^{13} ions/s was also used to minimize the effects of beam heating during implantation.

Table 1
Detailed implantation parameters for the diamonds implanted using the CIRA routine.

Implanted ion	Ion energy (keV)	Low fluence implantation (ions/cm^2)	High fluence implantation (ions/cm^2)
		Fluence component	Fluence component
^{12}C	150	0.40×10^{15}	2.80×10^{15}
^{12}C	120	0.26×10^{15}	1.83×10^{15}
^{12}C	80	0.22×10^{15}	1.53×10^{15}
^{12}C	50	0.12×10^{15}	0.84×10^{15}
Total fluence		1.00×10^{15}	7.00×10^{15}

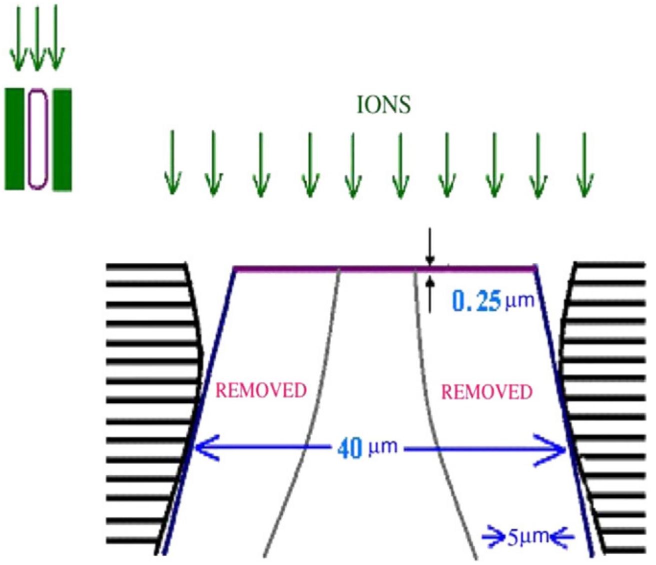

Fig. 1. Schematic diagram of implantation into a thin diamond edge, drawn roughly to scale. The inset shows the whole sample/holder sandwich, not to scale (the diamond would be much thinner). Possible lack of parallelism in the mating surfaces is suggested.

A pair of thin diamond slices was glued implanted edge against edge onto a copper support TEM grid. The samples were then thinned for conventional X-TEM at the Nelson Mandela Metropolitan University by Ar-ion milling using a Gatan Precision Ion Polishing System (PIPS, model 691) at 5 keV at a glancing angle of 5°. Electron transparent regions were achieved away from the ion milled hole along the glue line joining the diamond specimens, perpendicular to the implanted profile. Bright field images and electron diffraction patterns were initially recorded in a 200 kV Philips CM20 electron microscope with a point-to-point resolution of 0.27 nm.

Subsequently, FIB cross sections were extracted from two of the CIRA processed samples by using a Helios Nanolab 650 FIB-SEM. In this case the FIB lamella was removed from the implanted edge further away from the ion milled hole in a region where no Ar ion milling took place. The final FIB-SEM polishing was performed using Ga ions with decreasing energies from 30 to 0.5 keV. These lamellae were investigated in a double Cs-corrected JEOL JEM-ARM200F HRTEM equipped with a Gatan Quantum Image Filter with HRTEM point-to-point resolution of 0.11 nm.

In a supplementary experiment to be described later, a type Ib sample was implanted at room temperature at a single energy of 150 keV with a dose of 7×10^{15} ions cm^{-2}. In this case the implantation was done in the conventional plan view approach, and a FIB lamella was removed to study the as-implanted profile in cross-section on the JEOL JEM-ARM200F HRTEM. No annealing was done on this diamond sample.

3. Results and discussion

We show first the TEM micrograph of C^+-ion implanted diamond (natural, type Ia) with a low fluence of 1.00×10^{15} ions cm^{-2} at liquid nitrogen temperature and rapidly annealed at 1600 K (see Fig. 2(a)) as observed in a Philips CM20 TEM. The sample has a thin region (result of Ar ion milling) close to the edge showing a number of thickness fringes. The damaged diamond anneals back to crystalline diamond as shown by the corresponding selected area diffraction pattern (Fig. 2(b)).

The X-TEM micrograph in Fig. 3 is from the same sample as in Fig. 2, with one exception: this cross-section sample of the implanted diamond was obtained by focused ion beam (FIB) milling as described earlier and the images were acquired using a double Cs-corrected JEOL-ARM200F HRTEM. The sharp nature of the diffraction spots in the SAD pattern obtained within the window of the implantation depth of ≈250 nm indicates here too that the low fluence CIRA implant retains the crystalline diamond structure and no extended defects or amorphous carbon was observed which could be attributed to the radiation damage due to implantation.

In the micrograph of Fig. 3(a) planar defects are visible, from the surface to the bulk of the diamond sample (except where the edge is thinnest). Two types of defects are visible in this natural type Ia diamond and these are dislocation loops on three sets of inclined {111} planes and so-called "platelets" [7] on three sets of inclined {100} planes