# Transmission electron microscopy investigation of radiation damage caused by keV multi-implantation in single-crystal diamond.

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**Abstract**

An understanding of the types of defects produced during the doping/implantation of diamond remains essential for the optimization of high-temperature, high-power electronic applications. Thus this study focuses on investigating the nature of the radiation damage produced during the multi-implantation of carbon ions in synthetic type Ib and natural diamonds, using the CIRA (Cold-Implantation-Rapid-Annealing) routine. The implanted and annealed diamond samples were characterized using transmission electron microscopy. For low fluence implantations, the damaged diamond retains its crystallinity after annealing at 1600K while implanting using a high fluence, i.e., a fluence above the amorphisation-graphitization threshold, followed by rapid thermal annealing (RTA) at 1600 K, results in an amorphous carbon layer close to the surface.

## 1 Introduction

Diamond with its outstanding and unique physical properties offers the opportunity to be used as semiconductor material in future device technologies. Promising applications are, among others, high speed and high-power electronic devices working under extreme conditions, as e.g.high temperature and harsh chemical environment. With respect to electronic applications, a controlled doping of the material is necessary which is preferably done by ion implantation. This technique allows incorporation of foreign atoms in defined depths and with controlled spatial distribution which is not achievable with other methods. However, the ion implantation process is always associated with the formation of defects being able to compensate carriers. It is therefore of essential to understand the nature of defects produced under various implantation conditions. Previous studies [1, 2, 3] on the ion implantation doping of diamond using CIRA (Cold Implant Rapid Anneal) technique have shown that a critical fluence of about $5.2\text{x}10^{15}$ ions $\text{cm}^{-2}$ exists beyond which the diamond structure transforms into graphite. Below the critical threshold, the damaged diamond anneals to its pristine condition [1].

Similarly, Kalish et al.[4] 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 amorphised layer, mostly $sp^2$ bonded, converts to graphite upon annealing. Direct observations using X-TEM of keV ion implantation damage in annealed diamond have not, apparently, been attempted due to the difficulty of thin specimen preparation. However, recent studies involving the direct examination of defects in irradiated diamond by transmission electron microscopy [5] using MeV energies, have reported that diamond transforms to an amorphous carbon when a critical threshold is surpassed. The amorphous carbon transforms to a moderate crystalline graphitic region upon annealing for 24h at $1350^0$C.

## 2 EXPERIMENTAL DETAILS

Slices of ∼500$\mu$m thick were cut from a single crystal natural diamond parallel to the {110} plane. The slices were polished down to ∼40$\mu$m using a scaife. The implantation was carried out at iThemba-LABS (Gauteng), South Africa, using a Varian 200-20AF ion implanter. The diamond samples were $C^+$ implanted using ion energies and doses described elsewhere [1] with the dose rate of 1$\mu$A and they were tilted about $7^0$ to the incident beam direction so as to minimize the effects of channelling. Cross-sectional specimens for TEM observations were prepared as follows: cross-sectional slices of about 40 $\mu$m were implanted edge-on, at liquid nitrogen temperature, followed by rapid thermal annealing for 30 min, at 1600K, in an argon atmosphere. A pair of thin slices were glued edge against edge onto a copper support TEM grid. A 3 mm round disc was laser cut out around the copper grid. The samples were prepared for TEM study by Ar-ion milling using a Gatan Precision Ion Polishing System (PIPS, model 691) at 5keV at an incident angle of $5^0$ (See Fig. 1). Bright field images and electron diffraction patterns were recorded in a 200 kV Philips CM20 electron microscope with a point-to-point resolution of 0.27nm.

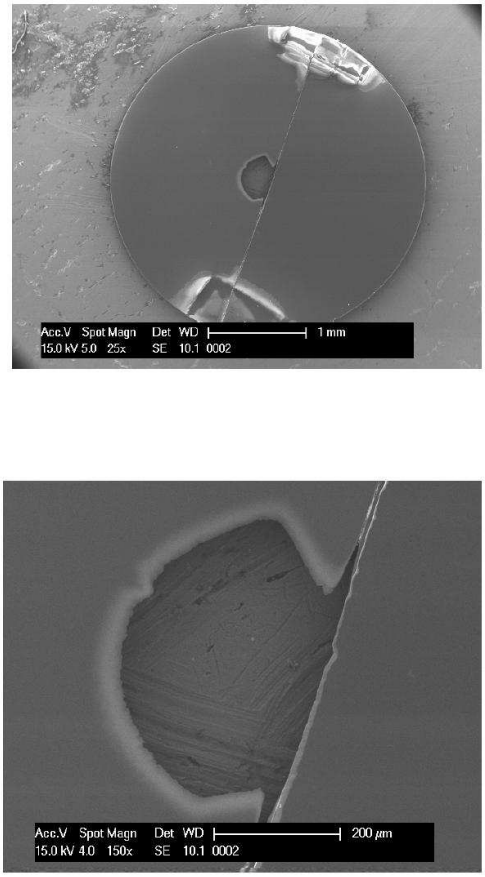


Figure 1: Scanning electron microscope (SEM) images of the cross-sectional ion milled diamond TEM sample. TEM investigation were carried out at the edge of the hole at the diamond/diamond interface.

## 3 Results and Discussion

The amorphous layer in Fig. 2 was recorded in diamond implanted with carbon ions to a high fluence of $7\times10^{15}$ ions $cm^{-2}$ at liquid nitrogen and rapidly annealed at 1600 K. Selected area diffraction patterns suggest a three layered structure i.e. graphite-amorphous carbon-diamond. The results indicate that the graphite layer lies from the implanted surface to ∼ 1000Å, while the amorphous layer runs from ∼ 1000 Å up to the end of the projected ion range. The dark defect contrast at the interface region between the amorphous implanted layer and diamond substrate is due to the implantation damage at the tail of the projected ion range as shown in Fig. 2.

The dark defect contrast at the interface region between the amorphous implanted layer and diamond substrate is due to the implantation damage at the tail of the projected ion range as shown in Fig.3. Therefore we can conclude that solid phase epitaxial regrowth (SPER) of diamond does not occur during annealing near the end of range where the density of defects is high and no extended defects were observed.

The TEM image (See Fig. 4) of a specimen implanted with carbon ions to a lower fluence of $1\times10^{15}$ ions $cm^2$ at liquid nitrogen and rapidly annealed at 1600 K does not exhibit any visible defects due to ion implantation and annealing. The damaged diamond anneals back to crystalline diamond as showed by the corresponding selected area diffraction.

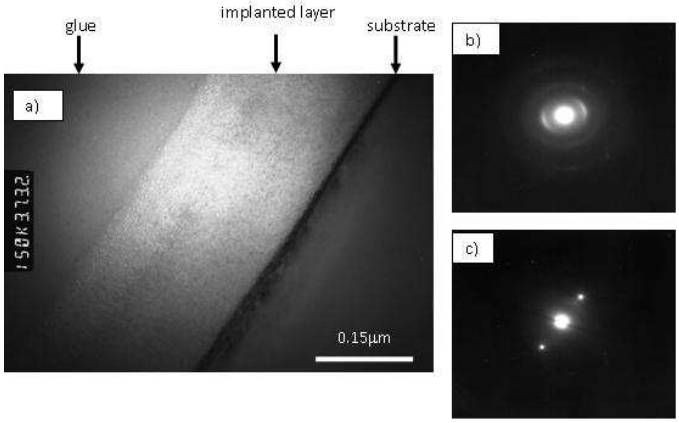


Figure 2: (a)Cross-sectional transmission bright-field TEM micrographs of diamond implanted with carbon ions to a fluence of $7\times10^{15}$ ion cm$^2$ at liquid nitrogen and rapidly annealed with SAD patterns from the implanted area (b) and diamond substrate (c). The SAD pattern (b) from the amorphous implanted layer exhibits the 002 arcs of graphite. The SAD pattern in (c) shows the 111 reflections of diamond.

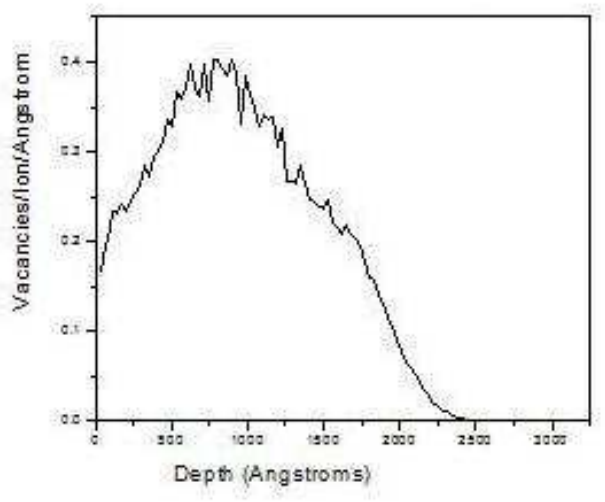


Figure 3: A SRIM-2003 simulation of the damage (vacancy) distribution produced by the carbon ion multi-implantation. The average projected range predicted by the Monte Carlo program is $\sim$ 2500Å while the highest level of damage lies at a depth of $\sim$ 1000Å.


Figure 4: Cross-sectional bright-field TEM micrographs of diamond implanted with carbon ions to a fluence of $1\times10^{15}$ ions cm$^2$ with corresponding selected area diffraction pattern. The sample has a thin region (result of ion milling) close to the edge showing a number of thickness fringes.

# 4 Conclusion

XTEM has been successfully used to characterize the radiation damage caused by keV multi-implantation in single crystal diamond. Diamond transforms to a graphite/amorphous-carbon layer when a critical threshold is surpassed whereas the damaged diamond anneals back to crystalline diamond when a fluence below the amorphization/graphitization threshold is used. Solid phase epitaxial recrystallization of diamond does not occur during the annealing near the end of range where the density is high and no dislocations were observed.

# 5 Acknowledgements

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