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# Cross-sectional transmission electron microscopy method and studies of implant damage in single crystal diamond

D. P. Hickey,[a] E. Kuryliw, K. Siebein, and K. S. Jones
*Materials Science and Engineering Department, University of Florida, Gainesville, Florida 32611-6400*

R. Chodelka
*The Gemesis Corporation, 7040 Professional Parkway East, Sarasota, Florida 34240*

R. Elliman
*Electronic Materials Engineering Department, Research School of Physical Sciences and Engineering, The Australian National University, Canberra Act 0200, Australia*

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Few transmission electron microscopy (TEM) studies of single crystal diamond have been reported, most likely due to the time and difficulty involved in sample preparation. A method is described for creating a TEM cross section of single crystal diamond using a focused ion beam and *in situ* lift-out. The method results in samples approximately 10 $\mu$m long by 3 $\mu$m deep with an average thickness of 100–300 nm. The total time to prepare a cross-sectional TEM sample of diamond is less than 5 h. The method also allows for additional thinning to facilitate high resolution TEM imaging, and can be applied to oddly shaped diamond samples. This sample preparation technique has been applied to the study of ion implantation damage in single crystal diamond and its evolution upon annealing. High-pressure–high-temperature diamonds were implanted with $Si^+$ at an energy of 1 MeV and a temperature of 30 °C. One sample, with a (110) surface, was implanted with a dose of $1\times10^{14}$ Si cm$^{-2}$ and annealed at 950 °C for 10 and 40 min. No significant defect formation or evolution was discernible by cross-sectional transmission electron microscopy. Another sample, with a (100) orientation, was implanted with 1 MeV at $1\times10^{15}$ Si cm$^{-2}$ and annealed at 1050 °C for 10 min. Prior to annealing, a heavily damaged but still crystalline region was observed. Upon annealing, the sample showed no signs of conversion either to an amorphous form of carbon or to graphite. This is unexpected as the energy and dose are above the previously reported graphitization threshold for diamond. Higher annealing temperatures and possibly a high vacuum will be required for future study of defect formation, evolution, and phase transformations in ion-implanted single crystal diamond. © *2006 American Vacuum Society.* [DOI: 10.1116/1.2209659]

## I. INTRODUCTION

There has been a growing interest in utilizing synthetic diamond for engineering applications since diamond was grown by Bundy *et al.*[1] The development over the past few years of increased production of both chemical vapor deposition (CVD)-grown and high-pressure–high-temperature (HPHT) man-made diamonds, along with reported high carrier mobilities[2] and the demonstration of diamond transistors,[3] have all driven this increasing interest.[4]

However, in order to be an effective semiconductor, single crystal diamond must be precisely doped to increase conductivity without graphitizing the diamond. Ion implantation has been used for decades to dope silicon for use in microelectronics. Similarly, ion implantation has been studied for over 30 years in diamond.[5]

In silicon, defects caused during ion implantation and the defect evolution have been studied by transmission electron microscopy (TEM). TEM would be an excellent method to further pursue a number of research questions in diamond, especially defect formation and evolution as the result of ion implantation and annealing, and the phase transformation from crystalline diamond to crystalline graphite.

TEM samples require thicknesses between 50 and 300 nm in order to be electron transparent. Creating these samples has typically been a very time-consuming process because of the properties of diamond.[6] Mechanical polishing and ion milling methods are typically used to create samples from CVD diamond films,[7] and high resolution TEM (HRTEM) has been used to image CVD diamond film defects.[6]

Due to the difficulty in creating TEM samples from single crystal diamond, few studies have been reported.[8] In the 1960s, TEM samples were prepared from natural diamond by oxidation thinning, which is flowing oxygen at 750 °C or carbon dioxide at 1350 °C over the diamond substrate, thereby gas etching the crystal.[9] However, this process does not protect the surface and is not selective of the area. Other disadvantages of this method are that the sample must be boiled in an acid mixture to remove the surface layer of graphite that forms and such high temperatures may anneal out defects present in the sample.[7] In 2001, plan view TEM studies were done on ion-implanted natural diamond.[10] Yin *et al.* has reported on the defects in a lab-grown HPHT diamond crystal studied using TEM as one method.[8,11] Additional TEM studies of HPHT single crystal diamond

[a]Electronic mail: dhickey@ufl.edu

whiskers[12] and particles[13] have been conducted. However, these sample preparation methods were not area selective in nature. Recently, Adams *et al.*[14] studied ion beam sputtering and damage in a single crystal diamond.

The focused ion beam has been used to create TEM samples in single crystal silicon and other materials faster than traditional methods.[15] Following FIB sample preparation, *ex situ* lift-out is common using micromanipulation tools, but *in situ* lift-out is also possible and preferable for the study of ion-implanted diamond. *Ex situ* liftout of diamond specimens is not preferable for two reasons. One is that the film commonly on the back of TEM grids is carbon, thus potentially compromising any electron-energy-loss spectroscopy (EELS) spectrum analysis of the ion-implanted diamond. Secondly, if the sample is not thin enough for high resolution work, it cannot be thinned further in the future. This may become an issue if the source material has been processed further. In addition, the diamond surface must be protected prior to creating the focused ion beam (FIB) cross section; otherwise the gallium ion beam could produce unrelated crystal damage as deep as 30 nm.[15]

The goal of this research is to develop a rapid method of creating cross-section TEM samples to study defect evolution in HPHT single crystal diamonds after growth, ion implantation, and annealing.

## II. EXPERIMENTAL PROCEDURE

HPHT single crystal diamonds, approximately $5\times5\times1$ mm$^3$, were provided by The Gemesis Corporation. A (110) oriented diamond was implanted with a dose of $1\times10^{14}$ silicon (Si) ions/cm$^2$ at an energy of 1 MeV and a temperature of 30 °C. A (100) oriented diamond was implanted with a dose of $1\times10^{15}$ Si ions/cm$^2$ also at an energy of 1 MeV and a temperature of 30 °C. Implantation of Si was performed in a tandem accelerator ion implanter. According to a SRIM-2003 simulation,[16] the damage should peak ($R_d$) at approximately 0.5 $\mu$m and the projected range ($R_p$) of the damage should be approximately 0.56 $\mu$m below the surface of the diamond. After implantation, a 1000 Å layer of $SiO_2$ was plasma-enhanced chemical vapor deposition (PECVD) deposited on the implanted surface, with the thermal exposure of the diamond being 310 °C for 1 min. The purpose of the $SiO_2$ layer is to prevent damage to the surface of the diamond from the gallium ion beam and to compositionally separate the carbon of the crystalline diamond from the conductive carbon coating applied next. Approximately 150 nm of carbon was evaporated onto the sample for conductivity and further protection of the sample surface.

The (110) oriented diamond, with a $1\times10^{14}$ Si/cm$^2$ implant, had TEM samples made (following the procedure discussed below) as implanted and also after annealing steps of 10 and 40 min at 950 °C in a flowing high-purity nitrogen ($N_2$) environment. The (100) diamond, with a $1\times10^{15}$ Si/cm$^2$ implant, had TEM samples made as implanted and also after 10 min at 1050 °C in a $N_2$ ambient.

Using an FEI Strata DB235 dual beam scanning electron microscope (SEM) and FIB, the sample area was selected. A $20\times2\times1.2$ $\mu$m$^3$ platinum box was deposited onto the chosen area. Using a 5000 pA ion beam sourced by gallium, a trench 6 $\mu$m deep was milled away on three sides of the platinum box. Tilting at 45°, an undercut using a 3000 pA ion beam released the sample wedge from the substrate bulk.

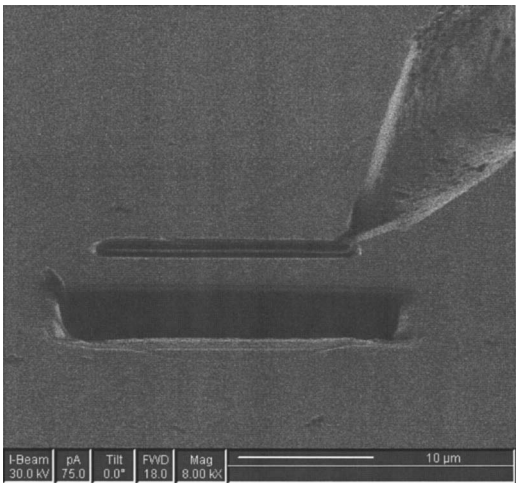


FIG. 1. *In situ* lift-out of diamond wedge, as viewed using the ion beam which is at a 52° angle to the stage. The diamond sample is approximately 3 $\mu$m deep on the far side, and the surface of the sample has been protected by a layer of platinum.

The Omniprobe Autoprobe 200™ *in situ* lift-out system was then inserted along with the platinum gas injection needle and placed on the corner of the sample. Platinum was deposited to attach the sample to the needle tip. The sample was then lifted out and retracted with the Omniprobe needle, as shown in Fig. 1.

The bulk sample was then removed from the chamber. An Omniprobe copper grid was inserted and adjusted in the FIB. The platinum needle and the Omniprobe needle, with the sample still attached, were reinserted into the FIB, maneuvered to the copper gird, and attached to the grid with platinum, using a 300 pA ion beam. Once attached, the Omniprobe needle was cut away from the sample using a 5000 pA focused ion beam. Both the platinum needle and the Omniprobe needle were then retracted.

At this point, the sample was approximately $15\times2\times2$ $\mu$m$^3$. Tilting the stage normal to the ion column, the sample was thinned, first using a 300 pA focused ion beam, then 100 pA, and final thinning was completed with a 50 pA beam. All ion beam energies described here were 30 keV. The sample was thinned from a +1° and −1° to normal, and alternating scan rotation setting of +1° and −1°, so that the end of the sample would be thin, moving to a thicker (approximately 200 nm) region at the base section attached to the grid. Figure 2 shows the thickness of the sample before and after the thinning process. The sample can then be viewed in the TEM without further processing.

## III. RESULTS

The single crystal diamond TEM samples produced by this method have been imaged in both regular resolution

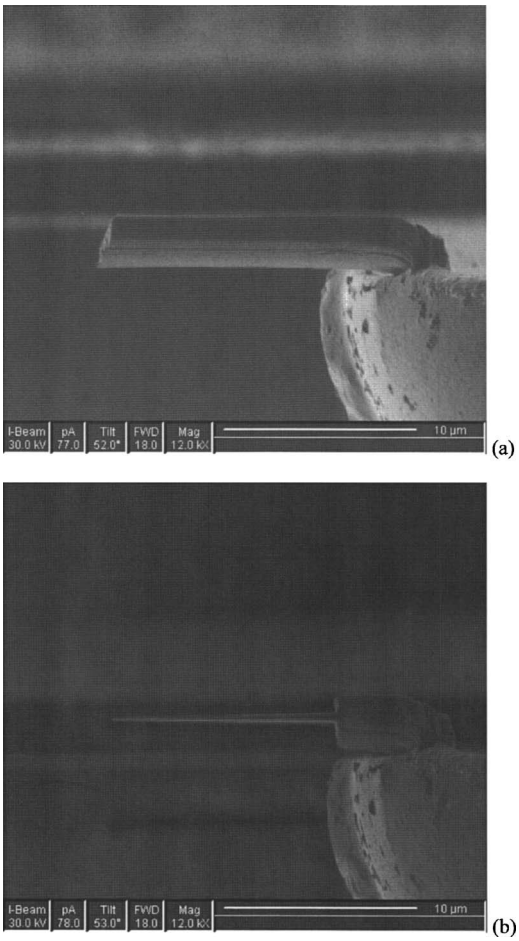


FIG. 2. Sample thickness before (a) and after (b) the thinning process.

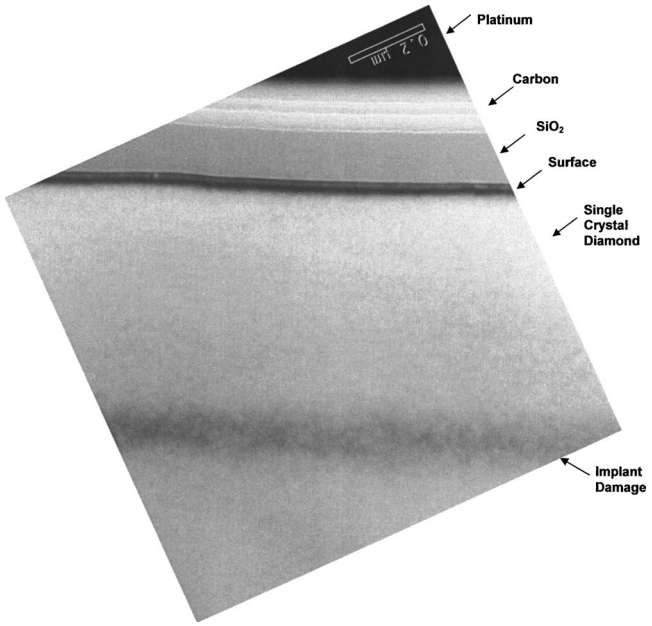


FIG. 3. TEM image of an as-implanted (110) single crystal diamond implanted with a 1 MeV $1\times10^{14}$ Si cm$^{-2}$ at a temperature of 30 °C.

TEM and HRTEM with good results. Figure 3 shows an image obtained on a JEOL TEM 200 CX clearly showing the layers of platinum, carbon, and silicon oxide above the diamond crystal. It also shows the implant damage from the $1\times10^{14}$ Si/cm$^2$ dose as it was implanted (without any anneal).

As this method has been developed to study the ion implantation damage evolution upon annealing, the results of preliminary studies will be discussed. The $1\times10^{14}$ Si/cm$^2$ diamond was annealed for 10 and 40 min at 950 °C in flowing $N_2$. Little to no change was observed in the damage layer during these times, as seen in Fig. 4. No extended defect formation or evolution is present. HRTEM lattice images and diffraction patterns showed that the sample was crystalline through the entire damaged region.

The $1\times10^{15}$ Si/cm$^2$ diamond was annealed for 10 min at 1050 °C in flowing $N_2$. Approximately 0.15 $\mu$m of the surface was etched, as seen in Fig. 5. The damaged region is clearly seen in both the as-implanted and annealed samples. A SRIM (Ref. 16) simulation shows that a 1 MeV implant of Si ions into diamond [using a density of 3.5 g/cm$^3$ and an $E_d$ of 45 eV (Ref. 18)] should produce a projected range ($R_p$) of approximately 0.56 $\mu$m and a damage peak ($R_d$) at approximately 0.5 $\mu$m. The TEM image in Fig. 5(a) reveals that this is a reasonable approximation of the damage. Additionally, energy dispersive spectroscopy (EDS) was performed to determine the chemical species present, the presence and depth of the capping layer, and the amount of gallium (Ga) implanted into the sample during the FIB procedure.

## IV. DISCUSSION

In creating these TEM samples, the total time per sample was less than 3 h, a significant reduction compared to traditional sample preparation techniques. In addition to time savings, another advantage over traditional sample preparation methods that is particularly good for rare substrate material (like single crystal diamond) is that very little material is needed, and the source of the sample can be reprocessed, increasing research efficiency and controlling costs at the same time.

This method differs from other FIB methods by accounting for the nuances of analyzing single crystal diamond. Carbon coating is often used to make insulating and semiconducting samples conductive for use in the FIB. However, as the point of this research will be, in part, to study the phase transformation of crystalline diamond, having a carbon layer deposited directly onto the diamond (carbon) substrate could compromise characterization methods such as EELS. To avoid this compromise, a layer of $SiO_2$ was deposited to differentiate the two layers. Figure 3 shows clearly the distinction between layers, proving this method to be successful. The top layer, in black, shows the platinum deposited to protect the surface from the Ga ion beam milling currents. The three layers of carbon coating, which protect the surface from the Ga ion beam damage, are clearly visible beneath the platinum. The next layer is silicon oxide, deposited to separate the carbon deposition from the carbon sample. Finally,

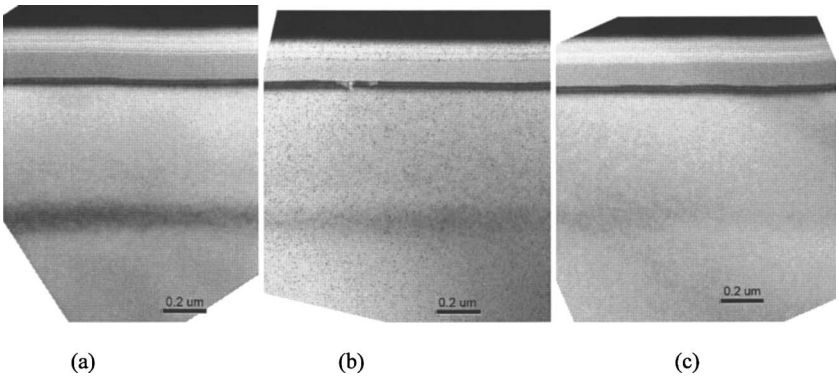


FIG. 4. XTEM bright field $g_{220}$ image of a (110) oriented single crystal diamond implanted with 1 MeV at $1\times10^{14}$ $Si^{+}$ $cm^{-2}$: (a) as implanted; annealed for 10 min (b) and 40 min (c) at 950 °C in a flowing $N_2$ environment.

the HPHT single crystal diamond is visible with the implant damage appearing as a dark band approximately 0.5 $\mu$m from the surface, as predicted by the SRIM-2003 (Ref. 16) simulation.

Other FIB sample preparation methods choose not to use *in situ* lift-out, but instead use an *ex situ* micromanipulation technique. This method involves removing the sample from the FIB after it has been released from the bulk, and then transferring the sample from the substrate to a grid by static forces. However, the grid is often backed by a carbon film. If this method were used for the single crystal diamond, characterization methods such as EELS could again be compromised due to the presence of carbon film behind the diamond sample.

In addition, the precision of this method allows accuracy and easy variation in the orientation of the cross section fabricated. This can be an issue since the traditional orientation of a silicon substrate, i.e., (100), is not always known for single crystal diamonds produced via the HPHT method. Site specific plan view samples are possible but require a different technique, and will not be discussed here.

Although this method has proven to be sufficient, it can be improved. HRTEM lattice images do show that the diamond lattice can be observed; however, image resolution can be improved by using lower ion beam energy on the final thinning cuts to impart less damage from the Ga ion beam. This method used a 30 keV beam during the entire thinning process. A direct 30 keV beam, according to SRIM (Ref. 16) (using a displacement energy of 45 eV per carbon atom[18]), created a damage peak at approximately 15 nm. However, the thinning beam was not direct, but only at a glancing angle, so the damage can be assumed to be less. Two characterization techniques were additionally used to determine that FIB damage was kept to a minimum. HRTEM showed that, even on the $1\times10^{15}$ $Si/cm^2$ implant, the sample stayed crystalline throughout its entire damaged region. Additionally, EDS showed that Ga (the ion used in this FIB process) was highly present in the platinum deposition layer (as is to be expected), but only in background amounts in the rest of the sample. Although these methods show that the Ga ion beam did not do extreme damage, even less damage could be achieved by switching to a lower energy ion beam for the final thinning cuts. For example, a direct 5 keV Ga ion beam would have a damage peak only 5 nm into the diamond lattice [according to SRIM (Ref. 16)] as compared to 15 nm caused by a direct 30 keV beam.

Two significant results are discernible from the data collected to date. First, the current annealing temperature and time regimes are too low or too short (respectively) to result in any significant defect evolution. Future studies will focus on higher temperature annealings (as suggested in recent literature by Vogel *et al.*[17]) in the range of 1400–1600 °C and will require the samples to be annealed in high vacuum. Figure 5 shows a bright field image of the diamond implanted with a Si dose of $1\times10^{15}$ $cm^{-2}$ both before (a) and after (b) a 1050 °C 10 min annealing in $N_2$. By lining up the damaged regions, the gas etching of the surface is evident—approximately 0.15 $\mu$m of diamond was etched from the surface, probably due to oxygen or water vapor present as a contaminant in the $N_2$ gas. This is the reason why high vacuum should be used for annealing diamond at higher temperatures.

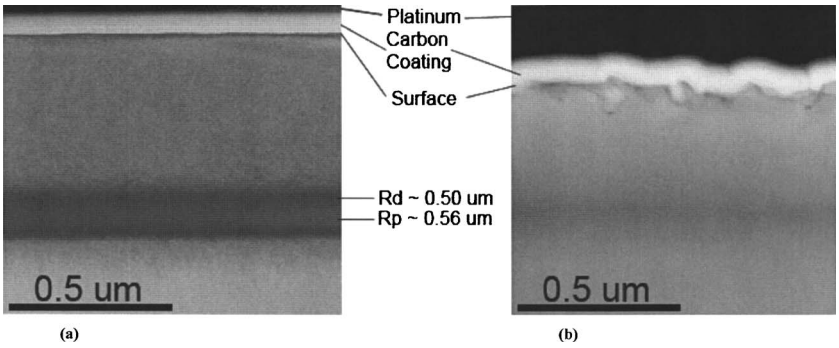


FIG. 5. XTEM bright field image of a (100) oriented single crystal diamond implanted with 1 MeV at $1\times10^{15}$ $Si^{+}$ $cm^{-2}$: (a) as implanted and (b) annealed for 10 min at 1050 °C in a flowing $N_2$ environment. By lining up the damaged regions, the gas etching of the surface is evident—approximately 0.15 $\mu$m of diamond was etched from the surface, probably due to oxygen or water vapor present as a contaminant in the $N_2$ gas.

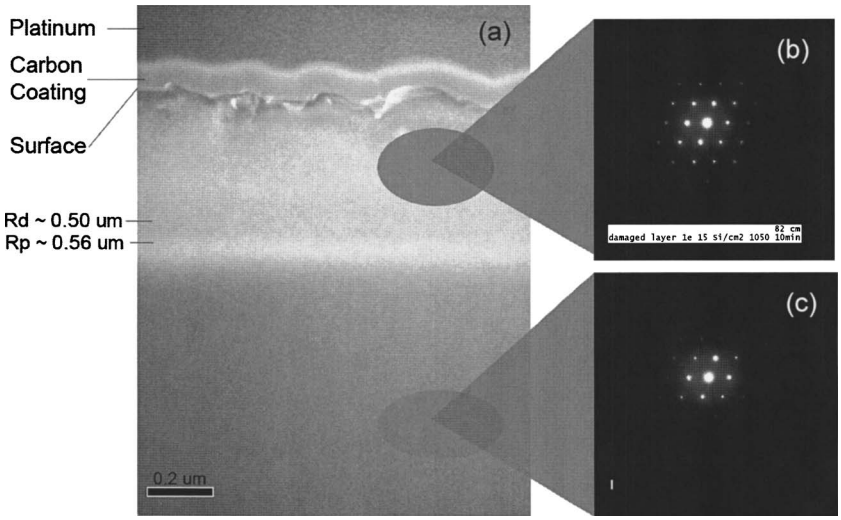


FIG. 6. XTEM of (100) oriented diamond after a 1 MeV at $1\times10^{15}$ $cm^{-2}$ $Si^{+}$ implant ($T_i$=30 °C) annealed at 1050 °C for 10 min: (a) XTEM image (labels denote platinum, carbon coating, and surface). (b) selected area diffraction pattern (SADP) of top region. (c) SADP of bulk.

The second significant result is contrary to some reported literature. Since direct TEM imaging of the damaged diamond lattice is uncommon, other measurements have been used to determine when the lattice repairs itself. The 1995 paper of Uzan-Saguy *et al.*[18] regarding the ion implantation threshold required for graphitization suggests a density of $10^{22}$ vacancies $cm^{-3}$ (assuming a diamond threshold displacement energy of 45 eV). In our studies the peak of the damage profile was below this result for the $1\times10^{14}$ $Si/cm^2$ dose but above it for the $1\times10^{15}$ $Si/cm^2$ dose. This suggests that clearly the $1\times10^{15}$ $Si/cm^2$ dose should have graphitized the sample to a depth of 600 nm. However, Fig. 5 seems to show a lessening of the damage upon annealing at 1050°C for 10 min. Weak beam dark field imaging of the same annealed sample (Fig. 6) confirms the crystal damage is still present and that the surface is single crystal diamond (as shown by the selected area diffraction patterns from the implant area), and not converted graphite. This agrees with the conclusion of Orwa *et al.* that MeV ion implants, even well above the graphitization threshold, can revert back to the crystalline diamond structure due to the high internal pressure.[19] In addition, this "threshold for graphite transition" is highly dependant on implant temperature.[20] Additional studies are necessary in order to determine the dependence of the graphitization threshold on implant temperature and the subsequent annealing kinetics of the damage layer.

## V. SUMMARY

In order to facilitate TEM sample preparation of single crystal diamond, a method using a focused ion beam (FIB) and *in situ* lift-out has been presented. After the surface has been protected by deposition of films, the FIB is used to create a sample wedge of the implanted surface. Next, the thin sample is removed and welded to a copper post on a TEM grid using an Omniprobe *in situ* needle, and thinned until the sample is electron transparent. This method has allowed the relatively rapid fabrication of TEM samples for single crystal diamond. TEM samples of as-implanted an annealed diamond samples were prepared. These experiments show that this method is sufficient for studying the defect evolution in single crystal diamond using TEM samples made from the FIB without imparting excessive damage to the crystal. It has been determined that higher temperatures and high vacuum annealing conditions must be pursued in order to study defect evolution using cross-sectional TEM. It is hoped that this technique will lead to better insight into carbon kinetics and future diamond device fabrication.

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