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Focused Ion Beam Implantation of Diamond

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ABSTRACT

The interaction between diamond and a 30 kV Ga⁺ focussed ion beam, commonly used for its functionalisation, has been studied. Electron backscattered diffraction identified the critical dose for amorphisation of the diamond surface at 2×10^{14} Ga⁺/cm². Scanning transmission electron microscopy results identified a 35nm amorphous carbon layer which, at higher doses, can swell up to 31% its own volume and accommodate a large quantity of gallium. Electron energy loss and energy dispersive X-ray spectroscopy further characterised this layer and identified both excess hydrogen and oxygen were contained in a stable amorphous carbon structure.

Diamond is a useful material for a range of applications given its diverse array of extreme material properties. A nano-fabrication tool required for functionalisation in many such applications is the Focussed Ion Beam (FIB). The FIB accelerates Ga⁺ ions towards a surface which, at a high dose can be used for milling or at a low dose for imaging. Examples of FIB-based fabrication of diamond include micro cantilevers¹⁻²; field emission tips³ electronic devices⁴, photonic devices including waveguides^{2,5} and lithographic patterning⁶⁻⁷.

The FIB has also evolved as a routine tool for the characterisation of nanoscaled diamond structures with techniques such as transmission electron microscope (TEM) lamella sample preparation⁸ and sub-surface imaging in both two and three dimensions⁹.

While it is widely known that energetic ion exposures change the diamond composition, density, bonding, crystallographic structure and electronic properties¹⁰⁻¹¹ few authors have studied these effects under the most common implantation conditions provided by (currently) the most common commercially available FIB systems, that from 30kV Ga⁺.

We present a study of 30kV Ga⁺ FIB damage in diamond to examine the corresponding changes in bonding, composition and crystal structure. This analysis will be an important guide for any application where a FIB system is used in the fabrication or analysis of diamond. It will also define the surface conditions that form a hard mask against a plasma etch, recently reported for the focussed ion beam hard mask (FIBHM) lithography technique⁶.

A series of FIB exposures between 10^{13} to 10^{18} Ga/cm² (at 30kV) were made using an FEI xP200 FIB system into a single crystal diamond with a {100} plane parallel to the surface. These implantation conditions were modelled with a Monte-Carlo simulation using TRIM software¹² shown in Figure 1.

Energy dispersive X-ray analysis (EDX) was performed to determine the relative gallium and carbon concentration near the surface using a Burker X-flash 5010 silicon drift detector interfaced onto a Hitachi s3400 scanning electron microscope (SEM). Monte Carlo simulations (using CASINO software) identified 3kV as an optimal accelerating voltage for the EDX analysis as its sampling profile best matched the gallium implantation profile predicted in Figure 1(a). Background subtracted signal integrals of Ga – L α (1.1 keV) and C – K α (0.28 keV) peaks, which could readily be detected at 3kV, were used for compositional analysis.

Electron backscattered diffraction (EBSD, using a TSLTM facility) was utilised to identify the critical dose for amorphisation of the diamond. An SEM (JEOL 7001F) illuminated the surface tilted 70° from the normal to the beam. At this geometry, Monte Carlo simulations (using CASINO software) identified 5kV as an optimal accelerating voltage for EBSD analysis as the sampling profile of the backscattered electrons best matched the vacancy distribution from the FIB implantation, shown in Figure 1(b). Patterns from all ion implanted diamond surfaces were acquired at the same camera settings and in a single run.

Scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) were used to analyse the cross section of an implanted sample (“Super STEM 1” Daresbury UK - C_s corrected VG STEM interfaced with an Gatan “ENFINA” EELS at the Super STEM laboratories,). Samples were prepared using a FIB based *in-situ* liftout technique⁸ with an initial electron beam assisted Pt deposition to protect the surface from additional Ga implantation. A final milling step at an accelerating voltage of 3kV and an angle of 5° from parallel to the lamella surface was applied in order to minimise FIB milling induced artefacts. The STEM was operated at 80keV, below the knock-on damage threshold for diamond at 86keV¹³. Compositional line scans used background subtracted signal integrals of EELS spectra from core loss edges; Fe-L, O-K, C-K, and Ga-L and low loss edges; α -bonded C, π -bonded C.

Figure 1: Depth profiles of (A) gallium ion ranges and (B) vacancies of 30kV Ga⁺ implanted into amorphous carbon based on TRIM monte-carlo simulations.

Figure 2: Surface effects of diamond irradiated with a Ga⁺ FIB at doses between 1 × 10¹¹ and 5 × 10¹⁷ Ga/cm². (a) EBSD patterns showing changes in crystal structure. (b) EDX results showing surface composition of Ga and C.

Figure 2 shows the near-surface structure (a) and composition changes (b) as a function of FIB dose. EBSD patterns in (A) indicate that at a dose of 3 × 10¹³ Ga/cm² the Kikuchi pattern appears unchanged relative to the unexposed “diamond” sample. At 1 × 10¹⁴ Ga/cm² the contrast appears faded indicating the crystal is damaged. Above 2 × 10¹⁴ Ga/cm² the Kikuchi pattern contrast has disappeared leaving an image resembling the uniform background of the camera. This pattern indicates the near-surface layer is amorphous, thus defining the amorphisation threshold at a 30kV Ga⁺ FIB dose at 2 × 10¹⁴ Ga/cm².

Figure 2(b) represents the composition change of the surface layer as a function of FIB dose analysed using EDX. Between 10¹¹ and 10¹⁴ Ga/cm² the carbon signal is seen to reduce gradually while no significant Ga signal can be detected. This is most likely a result of a density variation from vacancies introduced into the diamond lattice structure. At doses above 10¹⁴ Ga/cm² a gallium signal is observed and this increases up to a peak at about 10¹⁶ Ga/cm², while the carbon signal continuously reduces to less than half its original intensity. This result is explained by the continuous reduction of the carbon density due to an increased accommodation of the much larger gallium atoms in the amorphous carbon matrix. Such a peak gallium intensity has been observed previously by secondary ion mass spectrometry measurements to reach 38 at%¹⁰, the level of which is consistent with the (order of) magnitude of the reduced C signal. Above 10¹⁶ Ga/cm² the C and Ga intensities (compositions) plateau. This plateau in concentration has been reported to coincide with the onset of significant sputtering, where the damage profile reaches an equilibrium with the removal of surface atoms¹⁰.

Figure 3: (A) Bright field STEM image of a single crystal diamond sample exposed to a dose of $4.2 \times 10^{17} \text{ Ga/cm}^2$ over the area indicated. The image is elongated in the vertical direction to highlight the surface profile. (B) EELS profile the implanted diamond region defined in (A).

Figure 3 provides an analyses through a cross-section of FIB-implanted diamond. Figure 3A shows a bright field STEM image which is artificially elongated in the vertical direction to highlight the surface profile resulting from a $4.2 \times 10^{17} \text{ Ga/cm}^2$ FIB exposure over the area indicated in blue. The main features are the un-damaged diamond and the amorphous carbon layer “a-C”. Under the area defined for the exposure where sputtering is significant, the profile will broadly be representative of the equilibrium “plateau” compositions above 10^{16} Ga/cm^2 ¹⁰.

In Figure 3(a), under the area defined for the exposure the effect of sputtering can be seen to remove up to 37nm of the surface. Outside this area an amorphous carbon (a-C) surface layer is seen to extend beyond the field of view indicating it has been implanted with a dose higher than the amorphisation threshold, $2 \times 10^{14} \text{ Ga/cm}^2$. This implantation results from overspray of the beam whose intensity reduces as a Gaussian function of distance from the central beam ¹⁴. This a-C layer is 35nm thick at the extremities of the image, however, closer to the defined exposed area the thickness increases by 11nm, representing a 31% increase in volume. We expect that such significant swelling is due to the maximum gallium uptake seen at a dose of $\approx 10^{16} \text{ Ga/cm}^2$ (Figure 2(b)). Closer to the exposed area the surface profile is seen to decline as a result of sputtering as the dose rises above 10^{16} Ga/cm^2 .

Figure 3(b) shows the EELS composition depth profile across the white line in Figure 3(A) labelled “profile in (b)”. The C-K, σ -C and π -C signals clearly identify the amorphous carbon and diamond layers. For depths between 5 to 37nm there are approximately constant signals from C (C-K edge), π -C and σ -C. Across this depth range the significant contribution from π -C indicates the bonding is characteristic of amorphous carbon. The depth range of amorphous carbon is consistent with the vacancy distribution profile predicted in Figure 1(b). At depths greater than 43 nm the C-K (representing density) and σ -bonded carbon signal both rise while π -bonded carbon is reduced, results consistent with undamaged diamond. This result closely correlates with the vacancy distribution predicted in Figure 1(b).

Figure 3(B) also shows the Ga profile which increases to a maximum at a depth of 5nm and consistently decreases with depth to the diamond interface. An oxygen signal is seen to peak in

concentration in the outer 4nm of the film and also maintain a lower level throughout the remainder of the gallium rich amorphous carbon layer.

Figure 4 shows a low loss EELS spectrum with an edge characteristic of hydrogen-hydrogen bonding, from a region of the amorphous carbon layer at a depth of 15nm. A high composition of hydrogen-hydrogen bonding suggests that dangling carbon bonds (from the ion damage) are saturated by hydrocarbon bonds which would preferentially form as a more energetically favourable configuration. Thus the introduction of hydrogen would passivate these dangling carbon bonds stabilising the tetrahedral co-ordination of carbon atoms in the amorphous carbon matrix. This stabilisation of the sp^3 -bonded carbon may explain its ability hold a significant amount of gallium and associated strain (31% swelling) while maintaining its structure. The sources of the hydrogen and oxygen have not been confirmed.

Figure 4: Low loss EELS spectrum of from the gallium rich amorphous carbon region ~ 15 nm below the ion implanted diamond surface. The spectrum shows a peak characteristic of hydrogen – hydrogen bonding.

The findings give evidence of the mechanism responsible for the FIB hard mask used for patterning diamond. Diamond implanted with 30kV Ga^+ appears unique in its ability to accommodating a very significant quantity of gallium given to its ability to transform to an expanded amorphous carbon matrix while maintaining a stable structure, possibly owing to the presence of hydrogen. At the surface of this accumulation, the composition is predominantly gallium and oxygen with very little carbon, which presents a material non-volatile in the environment of an oxygen plasma. This surface defines a boundary condition for the on-going study of why FIB implanted diamond masks both oxygen and argon plasma etching, responsible for patterning with the FIBHM technique.

A 30kV FIB implantation incident normal to a diamond surface, the near-surface microstructure evolves with dose as follows:

- $< 3 \times 10^{13} \text{ Ga/cm}^2$ - diamond maintains its crystal structure
- $1 \times 10^{14} \text{ Ga/cm}^2$ - significant damage to the diamond crystal structure
- $2 \times 10^{14} \text{ Ga/cm}^2$ - complete amorphisation
- $1 \times 10^{15} \text{ Ga/cm}^2$ - maximum uptake of gallium by the amorphous carbon structure
- $> 1 \times 10^{17} \text{ Ga/cm}^2$ - onset of significant sputtering and formation of an equilibrium near-surface damage profile.

The resulting structure presents as an amorphous carbon layer which can swell up to 33% its own volume in order to accommodate a significant amount of gallium. The outer 4nm forms a surface

gallium oxide. The underlying amorphous carbon layer is ~43nm thick and contains gallium, oxygen and hydrogen-hydrogen bonds.

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