Low Dose Radiation Damage in Diamond from High Energy Electrons and Photons

T Nemakhavhani[1], R Andrew[1], JE Butler[2], SH Connell[1], MN Cook[1,3], R Erasmus[4], J Van Rooyen[5]

1. University of Johannesburg, Johannesburg, Mechanical Engineering, South Africa
2. Cubic Carbon Ceramics - Huntingtown Md, USA
3. Gem Diamonds, South Africa
4. School of Physics and Microscopy and Microanalysis Unit, Wits University, South Africa
5. Necsa, South Africa

E-mail: tnemakhavhani@uj.ac.za

Abstract. Radiation damage is of great interest in diamond. Diamond is so-called radiation hard and is a candidate for passive and active electronics in high radiation environments. Further, it is possible to treat diamond by radiation and annealing stages, so as to change its colour or introduce a favoured colour. The study of radiation damage is therefore well advanced in diamond. More recently, so-called quantum diamond is engineered by a low dose damage and ion implantation process. Our own interest in the matter of radiation damage in diamond arises from natural diamond recovery using the MinPET technique. This has a high energy photon irradiation stage to produce internal Positron Emission Tomography (PET) emitters, whose subsequent transient PET radiation yields 3D quantitative local carbon density distributions within kimberlite rock. We have therefore made a study of radiation damage in diamond in the limit of very low dose derived from a high energy mixed radiation field of photons and electrons. The process has also been modelled using Geant4. The major mechanism for displacement of carbon atoms is ballistic collisions derived from the primary and secondary electrons. One must also consider the damage due to the secondary carbon recoils. Then there is the various nuclear reactions and the secondary consequences of these. The primary damage created is the single neutral vacancy (GR1 defect). There are also the primary interstitials which can be the single dumbbell interstitial on cubic face centre (R2 defect) or the self-trapped pair of these (R1 defect). Finally there can be aggregates of these defects with each other as well as with pre-existing defects in the diamond (if these were present not too far from the radiation induced defect). As most of these defects are optically active, measurements were performed using UV-VIS absorption spectroscopy, IR absorption spectroscopy and very sensitive photo-luminescence (PL) spectroscopy at 77K. The results will be presented and discussed. The low dose experiments to characterise the MinPET diamond discovery system showed the damage creation was too low to be quantified.

1. Introduction

Radiation damage in diamond is a much studied subject, due to its importance as mentioned in the abstract, and also due to its complexity. For example, diamond does not anneal to a high quality lattice as silicon does, as one might have at first expected. If this were the case, there would be very high quality diamond both for the gem industry and for scientific and industrial applications on the market. Instead, one achieves high quality either by very superior and particular synthesis conditions in the case of synthetic diamond, or in the case of gems, there must be selection of the rarest specimens. Diamond is a metastable allotrope of carbon, and high temperatures require stabilising high pressure and inert environments to prevent surface reactions. However, even annealing experiments at high temperature and pressure (up to 2000

K and 5 GPa) do not mange to anneal the lattice to high quality [1]. Point defects that can be mobilised during annealing tend to form complexes or trap at other point and extended defects that are less mobile. The annealing behaviour of radiation damaged diamond is therefore strongly dependent on any pre-existing defects. This means that annealing can improve diamond to some extent, but usually, it is a treatment for colour enhancement. For example, a yellow diamond has single substitutional nitrogen (impurity) at trace levels. If vacancies are introduced by irradiation, and an annealing stage follows, then single vacancies which become mobile may then be trapped at the nitrogen (NV centre) and will endow the diamond with a pinkish colour. One does not entirely anneal out the nitrogen or the vacancies. Instead one has complexation and aggregation of defects. Experiments to understand primary radiation defects in diamond were therefore not entirely successful until they were carried out under conditions of low defect mobility (well below room temperature during irradiation) and in very pure and very high quality crystal specimens. It is now known that the most significant primary radiation induced defects are the single vacancy, known as GR1 (general radiation defect 1) and then the single interstitial, followed by complexes of these, such as the divacancy, the double interstitial, known as R2, V_2 and R1 respectively [2, 3, 4, 5, 6]. Then of course, with some annealing, there are yet higher order complexes of these, and depending on the presence of other pre-existing defects, complexes with them as well. The most important class of pre-existing defects which trap radiation damage is the nitrogen related defects. These are the single substitutional nitrogen mentioned earlier, N_s, the A-centre, which is two neighbouring substitutional nitrogen atoms and the B-centre, which is four nearest neighbour substitutional nitrogen atoms surrounding a vacancy. Of course the list is really very much longer. More recent articles on radiation damage in diamond can be studied [7, 8] including the references therein to track and expand on the statements made here.

These references and the references therein reflect many studies using low energy (few MeV range) electron irradiation; other charged particles; photon induced radiation damage, also in the low energy regime; and neutron induced damage, similarly with low energy neutrons. One may also find some studies at a very high energy, such as that relevant to the Tevatron or the Large Hadron Collider (GeV range). An interesting theoretical study using Monte Carlo style modelling of the damage may be found in the references [9, 10]. These studies connect to the low energy damage regime and progress out to 10 MeV.

In this paper we are interested in a very low dose regime, to understand the limits of detection of radiation damage in diamond. The presence of detectable defects is in a separate dose regime to that which could lead to an "altered" or a "treated" diamond, as might affect the natural diamond's properties or value as a gem. The energy regime of diamond radiation is raised to the 40 MeV level, and the theoretical modelling is much further developed than previously, deploying the well established particle tracking code, Geant4 [11, 12]. The relevant low dose is that dose that is used in the MinPET system [13] which activates Positron Emission Tomography (PET) isotopes within kimberlite rock for the later PET detector based sorting of diamondiferous from barren kimberlite in a online run-of-mine context. Here the primary electron beam energy is 40 MeV with a dose of $< 3 \times 10^{12}$ e^-/cm^2, and where a mixed radiation field (shower) of electrons, photons and nuclear reaction products develops within the kimberlite and the diamond. We shall call this mixed integral flux the "MinPET Dose" for the purposes of this paper.

2. Simulations, Experiments, and Results

The irradiation system consist of a primary electron beam energy with an energy of 40 MeV, which firstly impacts a thin (3 mm) tungsten slab leading to an electromagnetic shower, which develops further in the diamond target. There is also a hadronic component to the shower, or cascade, due to nuclear reactions (elastic and inelastic), delayed recoil following nuclear decay and also elastic coulomb scattering secondaries. The tungsten acts as a primary converter for bremsstrahlung radiation. It optimises the yield of photons in the Giant Dipole Resonance energy regime for the reaction $^{12}C(\gamma,n)^{11}C$, so that the photo-transmutation reaction yielding the ^{11}C PET isotope is maximised, so that ultimately, diamonds can be discovered in kimberlite as carbon density hot spots in a PET tomograph. Geant4 is used to track the histories of a large ensemble of such high energy electron initiated showers. The most important damage producing hadronic component is the carbon recoils themselves.

2.1. SRIM study of vacancy production by C-recoils

In the circumstances of this study, these are typically less than 1 keV in energy, but they are very effective as a secondary source of additional vacancy production, as they will have a large Rutherford cross-section and are very heavy. Figure 1 below shows how the SRIM [14] programme was used to generate the specific vacancy production as a function of incident projectile energy by these recoils as an interpolable set of points.

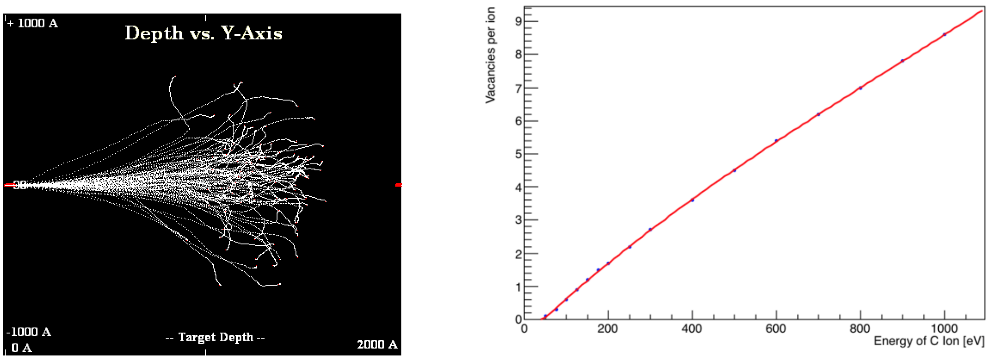

Figure 1: Left: A typical SRIM cascade for 100 keV carbon in diamond. There are 99 events with 215 vacancies per ion. The axes represent depth and transverse position in Angström units. Right: A section of the curve for vacancy production as a function of incident projectile energy.

2.2. Geant4 study of shower development and damage production

Geant4 can now be used to model the damage production. This includes the electromagnetic physics of the shower formation, and also the physics of the electron (and positron) components of the shower as they deposit energy and transfer momentum into the lattice, considering especially the screened relativistic non-ionising energy loss (SR-NIEL) [15]. The SRIM result discussed above is used in conjunction with Geant4. The Geant4 simulation gives the energy distribution of ion recoils, and the curve in Figure 1 then gives number of primary knock-on vacancies that are created from these recoils. Figure 2 below shows a visualisation of the primary electron beam and the shower development in the system described, and then also a 3D rendering of vacancy production in the diamond. Currently the hadronic component is not switched on in the simulation. A careful process of identifying which reactions are most significant to include is being done in parallel using the code FISPACT [16]. It is currently estimated that the nuclear hadronic component will contribute 20% to the vacancy production.

2.3. Experimental study of vacancy production using photo-luminescence

A synthetic diamond (type IIa) grown by the High Pressure High Temperature (HPHT) method with a low nitrogen concentration (around 10 ppb) and a high quality lattice (only a few dislocations overall) was used. It was irradiated as described above where the energetic core of the shower had an elliptical footprint with dimensions smaller than the sample. The dose was 600 times the “MinPET dose” described above. After irradiation the photo-luminescence (PL) signal from the single neutral vacancy (GR1) signal was studied. This is a peak at 741 nm. The excitation was via a 514.5 nm confocal laser / detector system and the samples were

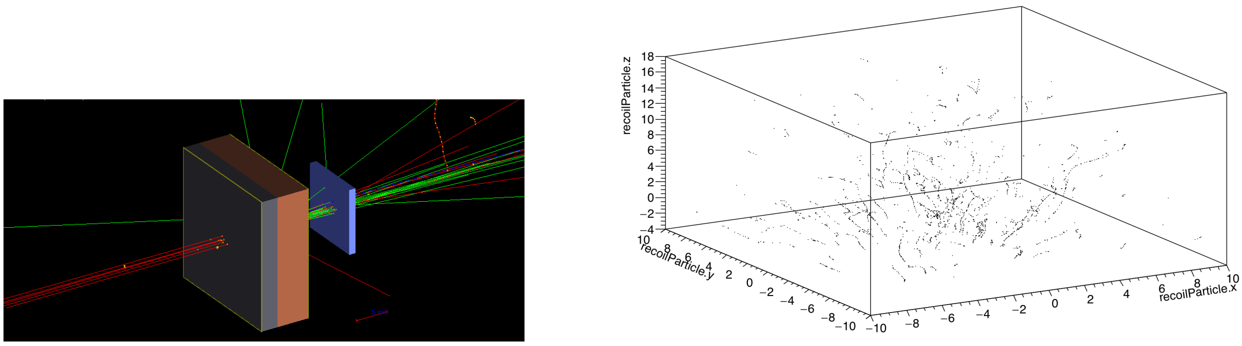

Figure 2: Left: A visualisation of the primary electron 40 MeV beam incident on the tungsten slab and the diamond with the shower development, and then also a 3D rendering of vacancy production in the diamond. Red - e^-, Blue - $^+$, Green - γ.

maintained at a temperature of 77K in order to enhance the intensity of the Zero Phonon Line (ZPL) relative to the phononic sideband components during the acquisition time of each spot. Spot analyses were conducted on a grid as shown in Figure 3 with acquisition times in the range of seconds per spot. This represents a near maximal sensitivity to the GR1 via PL. The GR1 PL peaks for each spot are also shown in the figure.

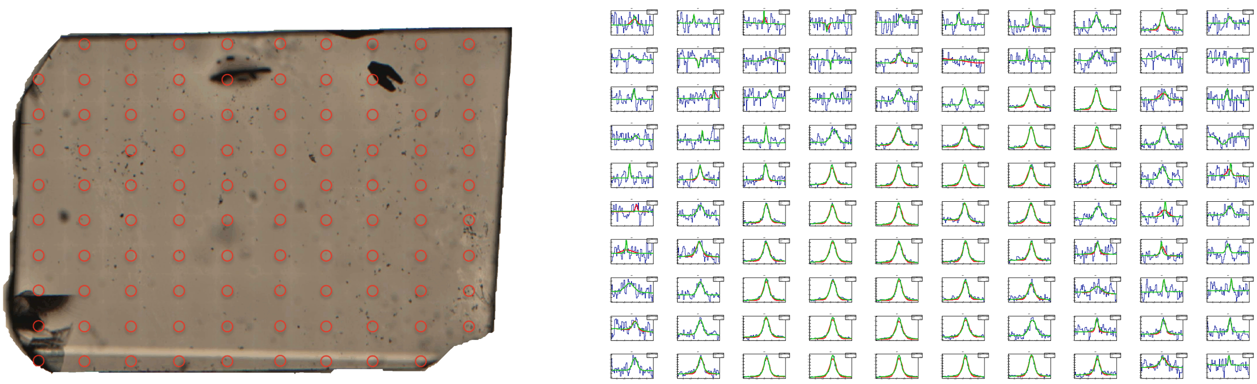

Figure 3: Left: The diamond sample (4mm×5.5mm) with positions indicated where the photoluminescence (PL) spot analyses were carried out. Right: The GR1 PL peaks for each spot. This represents a map of vacancy production by the electromagnetic shower.

The Figure 4 below shows the GR1 PL peak at 741 nm arising from a primary electron beam dose of 2×10^{15} e^-/cm^2 (600 MinPET doses). By scaling the noise statistics and considering a peak 600 times smaller, the conclusion is the GR1 concentration is near or below the minimum detection limit (MDL) in these experimental conditions. Figure 4 also shows a 3D reconstruction of the GR1 production concentration in arbitrary units. There is an effort to convert the production to absolute units. One method relies on the use of the Raman peak intensity acquired during the same experiment to normalise the intensity of the ZPL. There are several systematics to be considered. Another method involves the use of a standard sample. There is currently a tension of a factor of 10 between the Geant4 simulation of the absolute vacancy production and the GR1 PL measurement. Continuing experiments aim to remove the tension. In this case the Geant4 simulation will become a tool that connecting all the different damage production experiments at different energies, reconciling the effects of shower development, which allows then the sensible comparison of data points across all energies and primary projectile types.

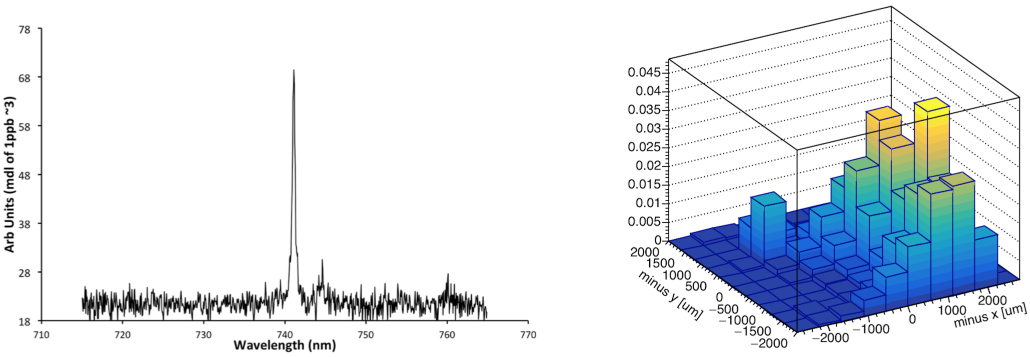

Figure 4: Left: Detail of the GR1 PL peak at 741 nm arising from a primary electron beam dose of 2×10^{15} e^{-}/cm^{2}. Right: 2D reconstruction of GR1 production concentration (arb. units).

2.4. Very low dose damage studies at high defect detection sensitivities

A selection of 10 natural diamonds was made, representing a variety of types (pre-existing defects). These are tabulated in Table 1. Essentially they will contain nitrogen impurities at different levels of aggregation in terms of A, B and N_s defects. These diamonds were studied by Optical Absorption (UV-Vis) as well as low temperature PL with different wavelengths of excitation as shown, and with different power levels. The irradiation was once again as in section 2. The characterisation was done before and after irradiation, to the dose shown in the table in "MinPET dose" units. The analysis conditions were chosen to provide maximal sensitivity in few spot analyses to a wide range of defects, those known to be associated with irradiation damage, and also as yet uncharacterised spectral features. It is not likely that the same spot was probed, before and after irradiation. This data will be discussed in more detail elsewhere. Many of these lines require aggregation of the radiation induced damage and the pre-existing defects. It is not considered reasonable that there could have been annealing conditions present in the experiments to enable this. One also considers that these diamonds have had a several billion year residence in the continental mantle. Here they would have had long term exposure to low dose irradiation from Naturally Occurring Radioactive Material (NORM). Calculations indicate this dose is about 1000 times the "MinPET dose". However, the physical conditions during the irradiation are very different. As such, on an aggregated defect molecular level, there will still be differences in the MinPET irradiation compared to the natural irradiation. Keep in mind that with some defects, for example the NV centre, it is possible to study a single isolated one of them by highly optimsed confocal PL techniques. This means the sensitivity to some defects is extreme, perhaps representing the finest example of the capacity to locate a needle in a haystack in all science. Accordingly, one notes by studying the table that there is a story that could be told of both pre-existing and new radiation related features, which for some stones contradicts others. As a whole, it is not certain one could say scientifically that the stones show evidence of non-natural irradiation. For example, in a gem scenario, one would not have the pre-irradiated information. Even with this information, the situation is not sufficiently clear.

3. Conclusion

We have presented a review of the main features of radiation damage in diamond. Following this we shown that one can model the spatial distribution of the production of vacancies, and also measure it, and that these two processes are converging. In due course, the tension in

Table 1: Summary of noticeable spectral changes due to the irradiation (PL at 77K).

Stone	Dose	Carats	Type	UV-Vis	488 laser PL	514 laser PL	633 laser PL
9	0	8.04	Ia		H3 slight incr, 787 appear	vvw 577 appearance	
2	0	3.55	Ia		H3 present		
6	1.6	8.06	IIa		3H appearance; stronger GR1, no NV, NV-	weaker NV,NV-, 612, weak broad 555, 630, stronger GR1	stronger GR1
8	1.9	7.12	IaA		H3, 700 stronger, 787 appear, No GR1	612 appearance	
5	2.1	4.75	IIa	weak 540 band	496, 3H, 612, 637 vvw, H3, slight GR1 Incr	GR1 vvw, broad 555, 600	weaker GR1?
7	2.6	5.83	Ia		H3 incr, No GR1		
3	2.6	7.9	Ia		H3 incr and ZPL splits?, 612, 676 appear, No GR1	612, 676 appear	787, 794 both present, no change
1	2.9	1.18	Ia		H3 always present, new band comes in on higher energy side after. Splitting or 3H? No GR1	weak broad band ca. 560 nm	679, 700, 787 appearance; 676 disappearance
10	3.5	3.58	IaAB		No GR1	535, 603, 640 appearance, 700 incr.	stronger 700;793 appearance
4	4	0.91	Iia	weak 540 band	broad at 555 appear, 496, 498.1, H3 incr, weaker NV-, GR1	weaker NV-, GR1, broad 555, 600 appear	no 787, 794 in either

the model and the measurement will not be significant, and at this stage one has a tool to compare all damage studies across all projectile types and energies, and come to a universal understanding of the primary damage creation. This is a significant contribution. Furthermore, we have shown that in the extreme low dose case, of the "MinPET dose", it is not yet possible to be sure a diamond was recovered by the MinPET technique. However, as knowledge of the damage mechanisms increases, and the technology for analysing these at low levels increases, it may ultimately become possible. This is a reflection of the extreme sensitivity at which defects can be detected by advanced techniques, as well as the complexity of the defect aggregation mechanisms. The total number of defects induced remains many orders of magnitude below the point at which any kind of alteration takes place that can be significant gemologically, for example changes that could be detected by any reasonable gemologically available instrument.

4. Acknowledgements
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