Effects of impurities and defects on the performances of synthetic diamond crystals when used as radiation sensors for medical applications

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Abstract. Diamond is attractive for medical applications due to its remarkable dosimetric properties. The dosimetric performance of a diamond crystal to radiation is however well recognised to be dependent on the types of defects and impurity levels within the crystal, and to date their influence on the performance of synthetic diamonds when subjected to low-energy X-rays and high-energy electron therapy beams has not been fully investigated. This study was therefore aimed at evaluating the dosimetric performances of synthetic diamonds when used as radiation sensors for both radiation types by highlighting some of the defect/impurity types that either enhance or degrade detector performance in order to select suitable crystals. The sensitivities of synthetic diamond crystals of various types (HPHT and CVD diamonds of optical grade (OG) and detector grade (DG)) were evaluated and compared based on their defect/impurity levels. The results of the study showed that the HPHT and OG diamonds had much higher levels of single substitutional nitrogen (N_s) impurities and were less sensitive compared to DG diamonds. The sensitivities of the diamond crystals to radiation were largely influenced, in particular by N_s impurities which act as recombination centres and degrade crystal performance in this study suggesting that N_s levels ought to be the foremost criteria used in the selection of a sensor material. As DG CVD diamonds have very low N_s impurities such crystals should be the radiation sensors of choice for medical applications.

1. Introduction

Diamond is attractive for medical applications due to its unique physical and dosimetric properties such as bio-compatibility, high sensitivity, high spatial resolution, non-toxicity, and more cost effective as it was shown in a previous study [1] that a single synthetic diamond probe could perform effectively in both low-energy X-rays and megavoltage electron beams. The dosimetric performance of a diamond crystal to radiation is however well recognized to be dependent on the types of defects and impurity levels present within the crystal - most arguably nitrogen - [2-6] , and to date their

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influence on the performance of synthetic diamond crystals when subjected to low-energy X-rays and high-energy electron therapy beams has not been fully investigated. In addition, different types and grades of synthetic diamonds exist – single crystal high-pressure/high-temperature (HPHT) diamond, single crystal (SC) chemical vapour deposition (CVD) diamond and polycrystalline CVD diamonds of detector grade (DG) and optical grade (OG) qualities – all of which perform differently and the reason is yet to be determined. This study was therefore aimed at evaluating the dosimetric performances (i.t.o. sensitivity values) of synthetic diamond crystals when used as radiation sensors for the above mentioned radiation types by highlighting some of the defect/impurity types that either enhance or degrade detector performance in order to select suitable crystals.

It should be noted that the use of natural diamond for medical applications is limited by the high cost and long delivery times, due to the scarcity of suitable stones [5], [7].

2. Experimental Details

Five commercially available synthetic diamond crystals of various types were investigated. These included one single crystal HPHT sample of dimensions 7.90 x 6.38 x 0.96 mm^3 and four polycrystalline CVD diamond samples (two DG (DGA1 and DGA2) and two OG (OGA1 and OGA2) samples) each of dimensions 5.0 x 5.0 x 1.0 mm^3. The opposite surfaces of each of the diamonds have been metallised as reported in a previous study [1] to provide the necessary ohmic contacts for voltage biasing and acquisition of the ionization signal. For quality control and the determination of defect/impurity types, the crystals were characterised using Raman spectroscopy and electron spin resonance (ESR). The Raman spectra were acquired using a Jobin-Yvon T64000 Raman spectrometer with the 514.5 nm line of an Ar^+ laser as excitation source. The ESR measurements were carried out with a Bruker ESP300E ESP spectrometer in a similar procedure as reported by this group [8].

The dosimetric responses of the diamond crystals to low-energy X-rays (25-32 kV_p) from a Senographe 500T mammography X-ray machine, and a 12 MeV electron therapy beam produced by a clinical linear accelerator (Siemens Primus) at the Charlotte Maxeke Johannesburg Academic Hospital (CMJAH) were measured. Each diamond crystal, biased at +50 V was encapsulated in, a probe housing as described in a previous work [1] and the probe, placed in its customised Perspex phantom was connected to a PTW-Freiburg UNIDOS E electrometer system operated manually in the 'charge' mode. The charge measured by the electrometer is defined as the response of the probe.

3. Results and Discussion

3.1. Raman Spectroscopy and ESR

Raman spectroscopy, which evaluates the material quality of diamond crystals showed only the characteristic diamond Raman peak at 1332 cm^{-1} over a linear background with no evidence of non-diamond component for all the crystals. The measured Raman widths (full-width-at-half-maximum (FWHM)) were 2.27±0.04, 2.60±0.13, 2.55±0.09, 2.56±0.09 and 2.41±0.06cm^{-1} for the HPHT, DGA1, DGA2, OGA1 and OGA2 crystals respectively. As the Raman width is an indication of the crystalline quality of diamond [9], i.e. a measure of the concentration of defects (such as point defects, crystal defects, grain boundaries, etc) it implies the HPHT sample having the smallest width (2.27 cm^{-1}) is the least defective crystal, and DGA1 having the broadest width (2.60 cm^{-1}) is the most defective crystal. The drawback of Raman spectroscopy is that it does not isolate defect types responsible for the inhomogeneous broadening of the diamond Raman peak.

Nitrogen, which is a commonly observed impurity in diamond, affects its electrical, optical and mechanical properties. It has been established that single substitutional nitrogen (N_s) is responsible for many performance characteristics of diamond radiation detectors [10]. ESR, which determines the concentration of N_s ($[N_s]$) gave values of 130, 3.5, 5, 42.9 and 71±2 ppm for the HPHT, DGA1, DGA2, OGA1 and OGA2 samples respectively. The much higher levels of N_s impurities of the HPHT and OG crystals compared to the DG samples observed in this study could be attributed to the technique normally used to grow diamond by the HPHT method and as for the OG crystals, we have

been informed that nitrogen is intentionally introduced during the growth of CVD OG diamond (private communication).

3.2. Dosimetric response of the diamond crystals – dose linearity and sensitivity

The linear response of a detector's signal with absorbed dose is a stringent requirement for medical applications. Dosimetric measurements for linearity evaluation and sensitivities determination included measurement of the response of each crystal as a function of absorbed dose on exposure to mammography X-rays and a 12 MeV electron therapy beam as shown in figures 1 and 2 respectively. Since X-ray tube peak kilovoltage (kV_p) and current-time product (tube loading, mAs) are two determinants of patient dose in mammography, with patient dose increasing either with an increase in kV_p or mAs, the absorbed dose was measured (with a PTW-Diados mammography detector – Type T60005 0735) as a function of kV_p (25 – 32 kV_p) at a constant tube loading of 200 mAs at the nominal distances used in routine mammography. For the 12 MeV electron beam, the measurements were done positioning the diamond probe in the Perspex phantom at the depth of dose maximum, d_{max} = 2.5 cm, at 100 cm source-to-phantom surface distance with an applicator defined field size of 10 x 10 cm^2 and the absorbed dose, (measured with a 0.6 cc Farmer-type ion chamber) was varied from 1.0 to 5.0 Gy by varying the number of monitor units from 100 to 500 using a dose rate of 3 Gy/min.

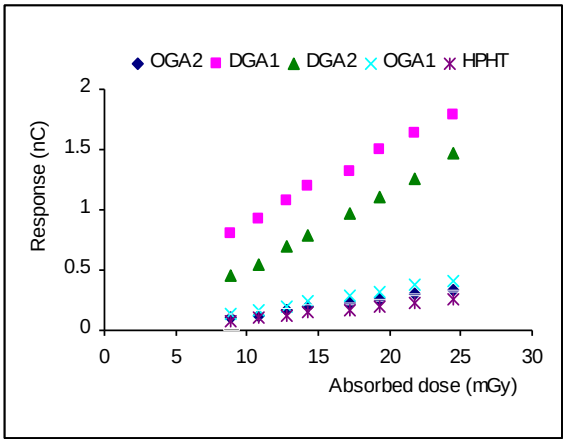

Figure 1. Response of the diamonds with absorbed dose at 200 mAs tube loading.

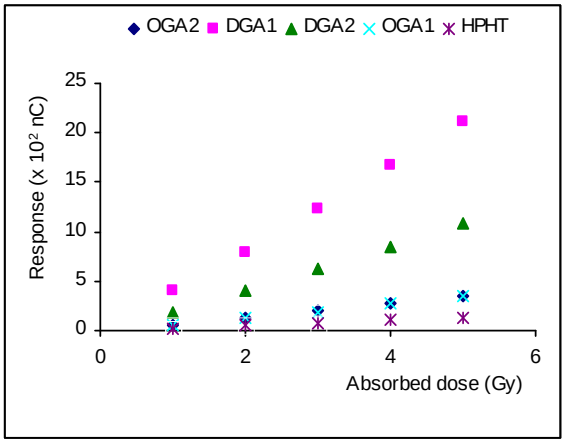

Figure 2. Response of the diamonds with absorbed dose for a 12 MeV electron beam.

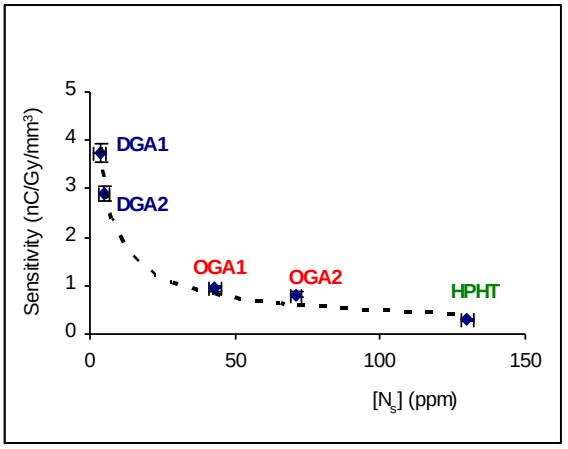

Figure 3. Variation of sensitivities (for the kV_p X-rays) of the diamonds with [N_s].

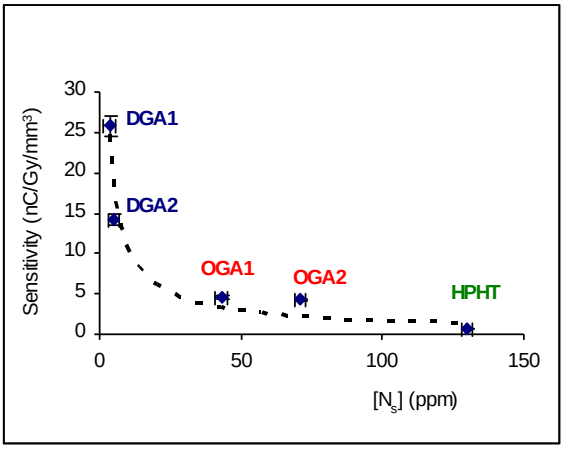

Figure 4. Variation of sensitivities (for the 12 MeV electrons) of the diamonds with [N_s].

As the sensitivity of a detector is defined as the collected charge, corrected for leakage, per unit absorbed dose and sensing volume [11], the slopes of the linear fits of figures 1 and 2 gave sensitivity values between 0.3 to 4 nC/Gy/mm^3 for X-rays and 0.7 to 26 nC/Gy/mm^3 for electron beams, where the detector volume of each crystal has been calculated as the product of the active area and thickness.

3.3. The role of impurity and defect levels of the diamond crystals

3.3.1. *Variation of sensitivities of the diamond crystals with [N_s]*. Figures 3 and 4 show the variation of sensitivities measured in X-rays and electron beams respectively of the diamond crystals with [N_s]. Both figures show similar trends or relationship between sensitivity and [N_s], with sensitivity decreasing as [N_s] increases. This is related to the observation that diamonds with N_s have high recombination efficiency which compromises the response [3]. Hence the figures show in general that N_s impurities in diamond act as recombination centres and degrade crystal performance (by reducing its sensitivity) when used as a radiation dosimeter. It is seen that the HPHT diamond with the highest [N_s] is the least sensitive while DGA1 with the lowest [N_s] is the most sensitive.

3.2.2. Variation of sensitivities of the crystals with defect levels. The sensitivities of the crystals were found to increase with Raman broadening (figures 5 and 6). As stated earlier, the Raman width indicates the presence and concentration of defects within a diamond crystal. Due to the presence of two inter-playing parameters, namely Ns impurities which act as recombination centres, and defect concentration, related to Raman width, the sensitivities of the crystals were then evaluated in terms of the ratio of Raman width to [N_s] in order to rule out the effect of [N_s]. Figures 7 and 8 show the variation of sensitivities measured in X-rays and electron beams respectively of the diamond crystals with Raman width per [N_s]. The increase in the sensitivity values of the crystals with the presence of defects could be attributed to one or a combination of two effects: the concentration of defects within the crystals and/or an increase in the interaction cross-section of diamond to radiation produced by the as yet unidentified defects within the crystals. Both effects result in the creation of more charge carriers suggesting in general that pure crystals or crystals with fewer defect levels may not function effectively as diamond radiation sensors. The particularly observed higher sensitivity of DGA1 to electron beams (causing the curve to deviate from linearity) could be attributed to the greater presence of a particular defect on the surface rather than within the crystal bulk making it more sensitive to electrons compared to X-rays.

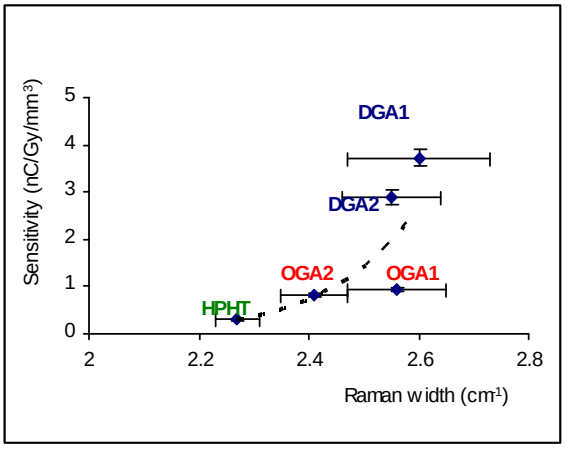

Figure 5: Variation of sensitivities (for the kVp X-rays) of the diamond crystals with Raman width.

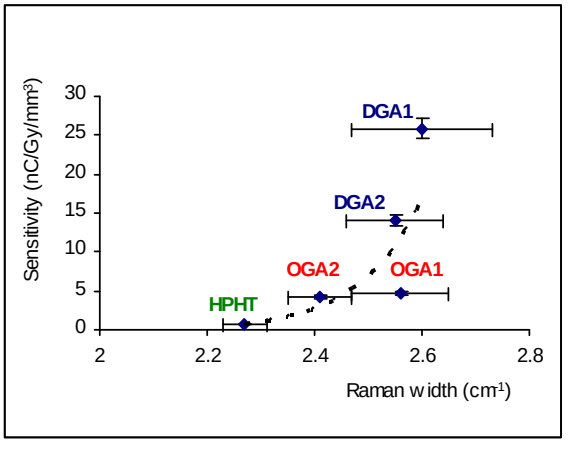

Figure 6: Variation of sensitivities (for the 12 MeV electron beam) of the diamond crystals with Raman width.

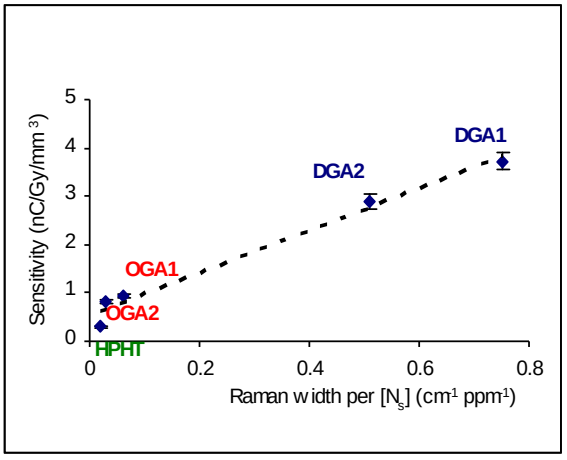

Figure 7: Variation of sensitivities (for the kVp X-rays) of the diamond crystals with Raman width per [N_s].

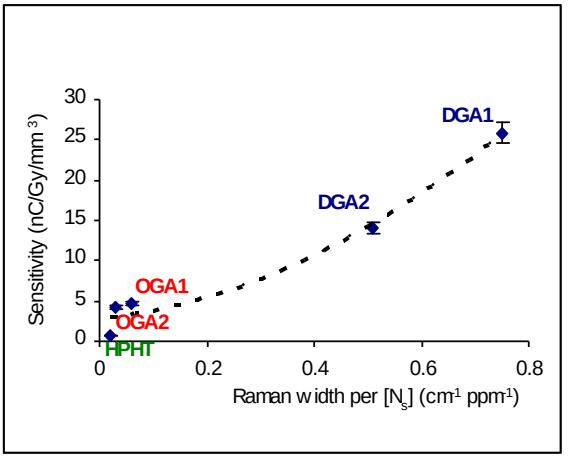

Figure 8: Variation of sensitivities (for the 12 MeV electron beam) of the diamond crystals with Raman width per [N_s].

4. Conclusions

In this study the HPHT and OG diamonds were found to have much higher levels of N_s impurities and were less sensitive compared to DG diamonds. The study has established that a diamond crystal with fewer defect levels may not function effectively as a radiation detector as the sensitivities of the diamond crystals were found to increase with defect density. The study thus concludes that once the defect type is identified, diamond could be selected or perhaps tailored made with defect and impurity levels which when used as radiation dosimeters could display optimum response. The sensitivities of the diamond crystals were largely influenced, in particular by N_s impurities which act as recombination centres and degrade crystal performance in this study suggesting that N_s levels ought to be the foremost criteria used in the selection of a sensor material. As DG CVD diamonds have very low N_s impurities such crystals should be the radiation sensors of choice for medical applications.

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