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Study of nitrogen content in HPHT diamond by Nuclear Reaction Analysis

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ABSTRACT

Nuclear reaction analysis (NRA) has been used for the determination of nitrogen content in diamond by monitoring the $^{14}\text{N}(\text{d},\text{p}_0)^{15}\text{N}$ nuclear reaction from a 1.4 MeV deuteron beam incident on the diamond samples. Results obtained in bulk diamond are compared to those inferred from infrared optical transmission measurements. Furthermore, nitrogen content has also been measured by NRA in diamond nanoparticles and in the light of these results we evaluate the conversion of nitrogen to nitrogen-vacancy (NV) complexes in both bulk diamond and diamond nanoparticles after a 2.4MeV-proton irradiation and subsequent thermal annealing.

Key words: diamond, color center, nuclear reaction analysis

I. INTRODUCTION

Over the past few years, the study of the negatively charged nitrogen-vacancy (NV^-) complex in diamond has been a very dynamic research field [1, 2] due to the interesting physical properties of this color center notably its photoluminescence stability and its optically detectable electronic spin resonance with a long coherence time. These properties confer to diamond a unique interest in applications such as quantum information processing, highly sensitive magnetometry [3, 4] and cellular imaging [5]. While these applications are based on the use of the NV^- center as isolated centers, there are applications that can benefit from a high density of NV^- centers in diamond such as ultrasensitive magnetometry [4, 6] at the micrometer scale, the realization of quantum hybrid circuits in which superconducting qubits are coupled to NV^- electron spins [7] or the use of diamond nanoparticles containing NV^- centers for bio-imaging [7, 8]. Under this impulse we have studied the optimal conditions for the production of a high density of NV^- centers in diamond based on the method of high energy particle irradiation of nitrogen-rich diamond and subsequent sample thermal annealing under vacuum [9]. The high energy particle irradiation is used to generate vacancies within the diamond matrix and the heat treatment allows vacancies to migrate until they are eventually trapped by nitrogen impurity atoms to form the NV^- centers. It is clear that for such a work a reliable knowledge of nitrogen concentration in our diamond samples is important. In the present work, we report on the use of nuclear reaction analysis (NRA) with a deuteron beam for the determination of nitrogen content in diamond with a sensitivity close to 15ppm. The results obtained allowed us to evaluate the conversion rate of nitrogen to nitrogen vacancy in both bulk diamond and diamond nanoparticles (NDs) related to our NV^- production method.

II. EXPERIMENTAL

Samples

In the present work we have studied both, bulk diamond monocrystals and diamond nanoparticles. The monocrystals were high-pressure high-temperature (HPHT) type 1b synthetic diamonds available as $(4.5 \times 4.5 \times 0.5)$ mm³ plates from Element Six. Two types of NDs were studied in this work: (a) commercial HPHT NDs from the manufacturer Van Moppes (Geneva) identified by the denomination ‘SYP 0-0.05’ with a specified median size of 25 nm and (b) diamond nanoparticles produced by detonation of an explosive mixture of a trinitrotoluene (TNT)/hexogen (RDX) (see fabrication details in reference [10]) with a typical size of about 5nm. For NRA analysis, these NDs were compacted in a thin layer (as thick as a few microns) by spin coating deposition of these NDs (suspended in ultrapure water) on a substrate. Three different types of substrates namely Si, GaAs and Ni have been considered in this work. The deposition is carried out for several hours in order to obtain a layer as thick as a few microns. Optical micrographs of the different ND layers formed on the different substrates (Figure 1) show that the adhesion of nanoparticles to the Si and GaAs substrates is not as good as that in Ni, which can be explained by the hydrophobic nature of these substrates. However full-scale views of these samples (see photos in the insets of figure 1) show that the layers formed on GaAs and Si are more homogeneous. In the pictures given in inset, the areas that have been scanned by the ion beam in NRA experiments are represented roughly by squares.

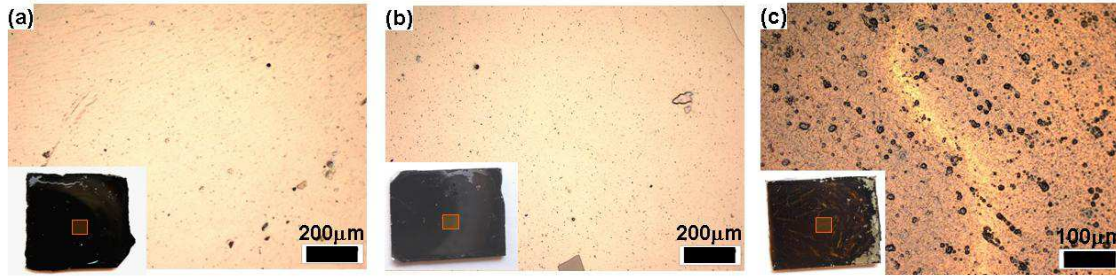


Figure 1: Optical micrographs of the ND layers deposited on different substrates namely: (a) $\sim 1\mu\text{m}$ ND layer on Si (b) $\sim 1\mu\text{m}$ ND layer on GaAs (c) $\sim 1\mu\text{m}$ ND layer on Ni. The corresponding full scale photos of the samples are given in the insets. The sample areas scanned in NRA are roughly represented by the squares on the photos.

Experimental NRA setup

Diamond mono- and nano crystals were analyzed by a 1.4 MeV deuteron ($^2\text{H}^+$) incident beam at a current value of 20 nA. A $1\times 1\text{ mm}^2$ collimator forms a rectangular beam spot on the sample surface. The beam incidence angle is 0° to the sample normal. Protons from the $^{14}\text{N}(d,p_0)^{15}\text{N}$ nuclear reaction allow us to detect nitrogen content with a probed depth of $7\mu\text{m}$ beneath the sample surface. Although the cross section of the nuclear reaction is two times higher at 1.8 MeV, we limited the incident energy to 1.4 MeV due to radioprotection constraints around the accelerator installation.

The proton signal was measured in coincidence using two 300 mm^2 full depleted PIPS (passivated implanted planar silicon) detectors, which we call detector A and B mounted in telescope to suppress spectral interferences. The $300\mu\text{m}$ fully depleted detectors are supplied in a transmission mount with a radial microdot connector. The detectors A and B are located at an angle of 150° from the beam direction and at a distance of 81 and 91 mm respectively from the sample (Figure 2). To prevent high counting rates on detector A due to backscattered deuterons, a

25 μm -thick Ni filter (purity of 99.9%) was placed in front of the detector. The Ni filter is mounted on a collimator of 16 mm in diameter. For detectors A and B, their corresponding active surfaces are 210 and 265 mm², with a solid angle of 32 msr.

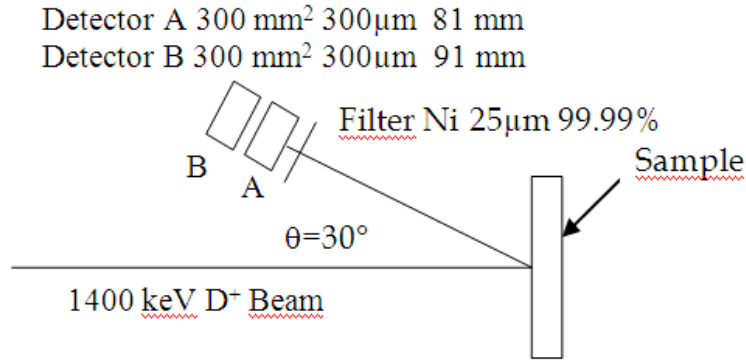


Figure 2: Experimental setup for the analysis of nitrogen concentration of bulk diamond monocrystals and diamond nanoparticles

Detector A allows measurement of the proton signal coming from the $^{12}\text{C}(d,p_0)^{13}\text{C}$ nuclear reaction. This signal is useful in estimating the mean thickness of the sample traversed by the ion beam, which is essential when measurements are performed on thin films of nanodiamonds. Protons emitted by the $^{12}\text{C}(d,p_0)^{13}\text{C}$ reaction are stopped in detector A while protons from $^{14}\text{N}(d,p_0)^{15}\text{N}$ are transmitted through it. The energy losses of emitted particles through the nickel filter and detector A are summarized in table 1 [12].

Nuclear reaction	E_S (keV)	E_{T-Ni} (keV)	E_{D-A} (keV)	E_{D-B} (keV)
$^{12}\text{C} (d,d) ^{12}\text{C}$	744	0	0	0
$^{12}\text{C} (d, p_0) ^{13}\text{C}$	3249	1600	1600	0
$^{14}\text{N} (d, \alpha_0) ^{12}\text{C}$	9909	0	0	0
$^{14}\text{N} (d, p_0) ^{15}\text{N}$	8667	8000	3500	4500
$^{14}\text{N} (d, p_{1+2}) ^{15}\text{N}$	3887	2500	2500	0
$^{29}\text{Si} (d, p_0) ^{30}\text{Si}$	7200	6400	4800	1600

Table 1: Emitted energies (E_S) in the near surface of the sample, transmitted energy (E_{T-Ni}) through the nickel filter and deposited energies in detector A (E_{D-A}) and B (E_{D-B}) for the main nuclear reactions at 150°

Detector B whose signal is set in coincidence with that of detector A allows measurement of the proton signal coming from $^{14}\text{N}(d, p_0)^{15}\text{N}$ by eliminating parasite signals. Before any NRA measurement was performed on ND films, the signal coming from the GaAs and Si substrate has been monitored in order to evaluate any parasite signal coming from the substrate. For silicon substrate, a relatively high signal in the corresponding $^{14}\text{N} (d, p_0)^{15}\text{N}$ energy channels of the B detector spectrum is detected (2 counts per μC). This high count rate may be due to high energy proton emission from $\text{Si}(d,p_x)$ nuclear reactions. The protons with highest energies come from the $^{29}\text{Si}(d,p_0)^{30}\text{Si}$ nuclear reaction and contribute to the background measured on the detector B as seen in table 1. The count rate per unit charge coming from GaAs substrate was measured for a charge of $100 \mu\text{C}$ and is found to be 0.06. It may be considered negligible with respect to that coming from the sample. This is why we have selected the GaAs material as the most suitable substrate for NDs. For a $0.2 \mu\text{s}$ coincidence time window, the NRA spectrum in figure 3b shows the main presence of the $^{14}\text{N} (d, p_0)^{15}\text{N}$ peak together with an erratic coincidence signal at low-

energy. The detection limit (DL) of nitrogen concentration in a 1 μm thick ND film on GaAs substrate is about 15 atomic ppm. DL is calculated from the formula $DL = 3 \times S_{\text{Background}} \times Fc$ where $S_{\text{Background}}$ is the signal per unit charge in the region of interest for nitrogen measured on the GaAs substrate and Fc the calibration factor in at.ppm per count and unit charge.

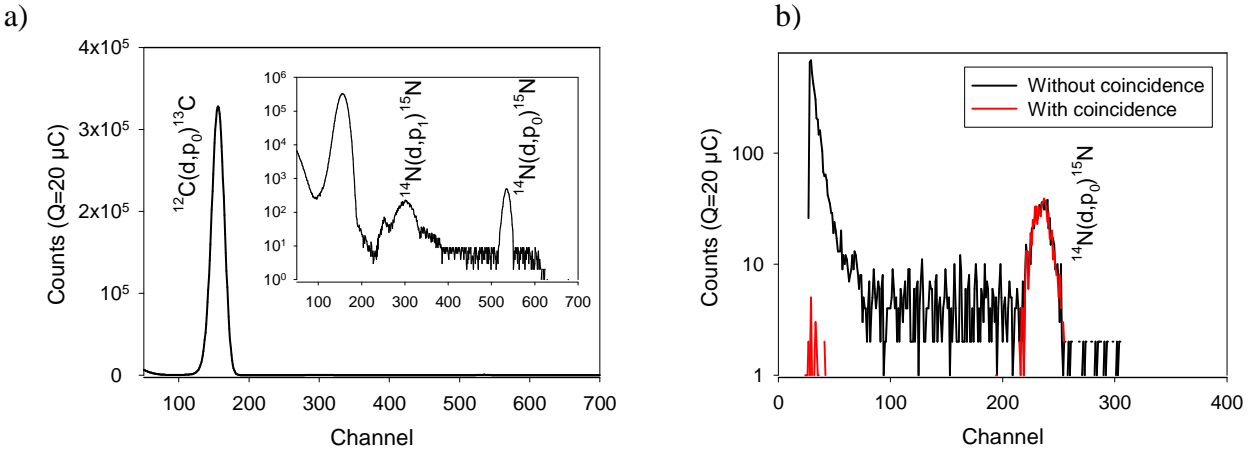


Figure 3: The NRA spectra recorded for ND films on GaAs substrate with (a) detector A and (b) detector B in coincidence or not with the detector A

Infrared transmission measurements were performed at room temperature with a Bruker Vertex 70 FTIR spectrometer employing an instrumental resolution of 1 cm^{-1} and an aperture diameter of 1.5 mm. The characterized samples have a plate shape and both sides are polished to avoid light scattering. The optical configuration used for the measurement includes a Globar source, a Ge/KBr beamsplitter and a DLaTGS/KBr detector.

II. RESULTS

Accuracy of the measurement technique

The accuracy of our NRA methodology in determining nitrogen content by monitoring the $^{14}\text{N}(d,p_0)^{15}\text{N}$ was tested on two nitrogen compounds: AlN and Si_3N_4 bulk materials. The nitrogen concentration is calculated by using nuclear cross section data from SigmaCalc [11] The

measured nitrogen concentrations in AlN and Si₃N₄ samples are respectively (51 ± 2) at.% and (59 ± 4) at.%, which correlates well with the expected theoretical concentrations.

In addition to this, the accuracy of the carbon signal measurement was performed by analyzing a glassy carbon sample. The carbon signal measured (79.5 ± 3.5 counts/μC) and that estimated (80.6 counts/μC) by SIMNRA [13] with ¹²C(d,p)⁰¹³C data cross section of Kokkoris [14] were found to be in excellent agreement. This validates the use of the ¹²C(d,p)⁰¹³C signal for estimating the thickness of the ND layer traversed by the analysis beam.

Nitrogen concentration in bulk samples

NRA was performed on both faces of two bulk diamond samples. Indeed, we must take into account the fact that only the first 7μm beneath the surface are probed by NRA. The results are presented in table 2. The values found are above 300 ppm which is higher than the value specified by the supplier (i.e. less than 200 ppm). Moreover, different concentration values are obtained on both faces of sample 1, which highlights the variation of the nitrogen content along the depth. In addition to this, concentration values obtained for sample 2 are lower than those obtained for sample 1. This underlines the variation of the mean nitrogen concentration from one sample to another.

Sample	NRA measurements [N] (at. ppm)		Infrared measurements [N] (at. ppm)
	Face 1	Face 2	
1	440±6	383±5	372±19
2	338±5	347±5	328±16

Table 2: Concentration values measured in two bulk type-1b HPHT diamond samples by NRA and FTIR.

FTIR measurements were performed on the same diamond samples in order to infer the nitrogen concentration based on the relationship established in reference [15] which links the strength of the characteristic 1130 cm^{-1} absorption peak caused by single substitutional neutral nitrogen atoms to the concentration of these atoms measured independently by electron paramagnetic resonance. According to this relationship, an absorption coefficient of 1 cm^{-1} for this particular peak relates to 22.0 ± 1.1 ppm of single substitutional nitrogen in the diamond lattice.

Infrared transmission curves were collected on two different double-side polished diamonds between the range of $100\text{-}6000\text{ cm}^{-1}$. The curves obtained have been normalized by the transmission value measured between $5000\text{-}6000\text{ cm}^{-1}$ where defect-related optical absorption is expected to be negligible. The normalized transmission values are then converted to absorption coefficient values by considering the following formula: $\mu = -\frac{1}{l} \ln(T)$ (1)

where l is the sample thickness and T is the normalized transmission value. l is taken to be equal to the sample thickness i.e. $500\mu\text{m}$. The results obtained in the one-phonon region ($900\text{-}1500\text{ cm}^{-1}$) are presented in figure 3.

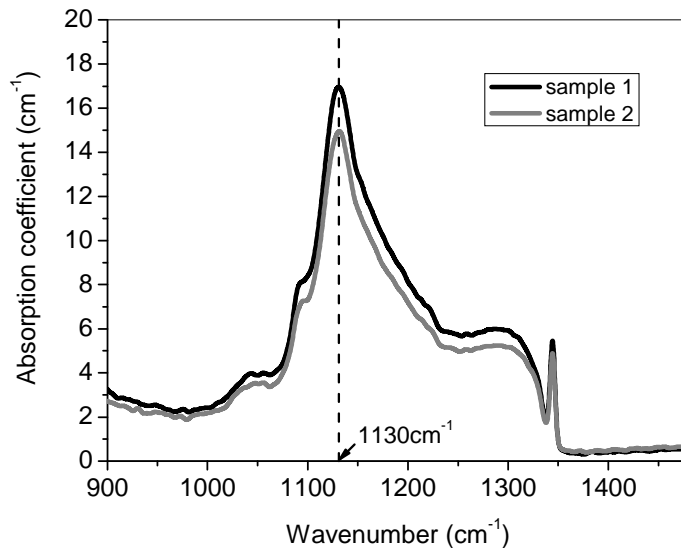


Figure 3: One-phonon region of the FTIR spectra of two type 1b bulk diamond samples.

In this region, we observe the characteristic absorption produced by neutral single substitutional nitrogen. The absorption coefficient at 1130 cm^{-1} allows us to determine the nitrogen concentration as discussed earlier. The calculated values are presented in Table 1. These values can be viewed as the mean concentration along the depth of the diamond sample. They are consistent with NRA results, thereby validating the use of NRA for quantifying nitrogen in diamond. Furthermore, infrared measurements carried out on 4 other type-1b diamond samples (spectra not presented here) allowed us to check that the mean nitrogen concentration varies between 300-450ppm.

NRA performed on nanodiamonds

The mean nitrogen concentration in HPHT NDs (labeled ND-HPHT 1 and ND-HPHT 2) and detonation NDs (labeled ND-DETON 1 and ND-DETON 2) are found to be about 0.6% and 3%, respectively (Table 3).

Sample designation	Measured sample thickness (μm)	Nitrogen concentration (at.%)
ND-HPHT 1	$2.20 \pm 0,07$	$0.62 \pm 0,03$
ND-HTHP 2	$0.93 \pm 0,03$	$0.62 \pm 0,05$
ND-DETON 1	$0.12 \pm 0,01$	$3.22 \pm 0,28$
ND-DETON 2	$1.40 \pm 0,04$	2.84 ± 0.20

Table 3: Nitrogen concentration values determined by NRA for different ND layers deposited on GaAs substrate

For HPHT NDs, the nitrogen concentration value of 0.6 at% is surprisingly high compared to the value specified by the manufacturer which is between 0.01%-0.03%. To check the possibility that air inclusions eventually present in the ND layer may affect the results, the ND layer with its

substrate was heated at 130°C/1h under argon atmosphere. After this treatment, the sample was analyzed again. The difference between measured nitrogen concentration before and after annealing under argon flux is within experimental uncertainty. So we conclude that the nitrogen concentration measured by NRA is indeed the nitrogen content in NDs.

On the other hand, the nitrogen concentration values obtained for the detonation NDs agree well with the values given in reference [16] obtained by spatially resolved electron energy loss spectroscopy (EELS) performed on similar NDs (2.7 ± 0.5 at.%). Furthermore, the EELS study has also been able to locate the nitrogen atoms within the nanodiamond core. The high nitrogen content in such NDs can be associated to the presence of nitrogen in the TNT/DRX explosive mixture.

III. DISCUSSION

To sum up the previous results, concordant concentration values have been measured by NRA and FTIR in bulk diamond and were found within the range of 300-450 ppm. The NRA technique measures the concentration of nitrogen atoms regardless of their position in the crystal lattice, whereas the FTIR technique measures the concentration of nitrogen in substitutional sites. The congruence of results between NRA and FTIR techniques supports the hypothesis that a high fraction of nitrogen atoms is located in substitutional sites within the diamond lattice.

NRA has also been successfully implemented to measure the nitrogen content in HPHT diamond nanoparticles and concentrations of ~ 0.6 at.% have been measured.

In the light of these data, it is interesting to evaluate conversion rate of N to NV (i.e. the concentration ratio of NV relative to N, $[NV]/[N]$) from data given in reference [8] for 30 nm HPHT ND nanoparticles from the same supplier (Van Moppes, Geneva) and from data in reference [9] for bulk type 1b HPHT diamond from Element Six. A mean number of 7 NV

centers was reported for 30nm HPHT NDs which have been irradiated with 2.4MeV protons at a fluence of $5 \times 10^{16} \text{ cm}^{-2}$ and afterwards annealed for 2 hours at 800 °C under vacuum [8]. Considering spherical NDs, a nitrogen concentration of 0.6 at.% is equivalent to about 15000 nitrogen atoms inside 30nm-sized NDs yielding a $[\text{NV}]/[\text{N}]$ ratio of about 5×10^{-4} . For bulk type Ib diamond, the concentration reached for 2.4 MeV proton-irradiated samples at the same fluence as above and which have been annealed under vacuum at 800 °C during 1h is around 3×10^{-3} (taking $[\text{N}] = 375 \text{ ppm}$) [9]. It can clearly be seen that the N to NV conversion rate is lower in NDs. Surface effects in NDs can be held accountable for this result. It has been reported in that defects are stable only within the core region of NDs, the remaining ones annihilating at the surface without forming NV centers [17]. Because of this, the probability of NV center creation is expected to vary inversely to the square of the particle radius for small sized nanoparticles ($\leq 10 \text{ nm}$). All these reinforce the idea that a better strategy to create small NDs with a maximum number of NV centers is to generate them in larger-sized NDs and to reduce their size afterwards by milling for example.

III. CONCLUSION

In this work we show that NRA has been successfully implemented to measure the nitrogen content in both bulk diamond crystals and diamond nanocrystals. In the former case, the NRA results are consistent with infrared transmission measurement both giving concentration values in the range of 300-450ppm. In the near future, the NRA channelling technique will be implemented to prove experimentally that the nitrogen atoms are preferentially located in substitutional carbon sites. In the diamond crystallographic structure, only the angular scans of the $\langle 110 \rangle$ axis and (110) plane would inform us about the presence of N atoms in interstitial

sites. For HPHT NDs, the estimated concentrations are found to be around 0.6 at.%, one order of magnitude higher than the values specified by the supplier. Based on these results, we furthermore show here that the conversion rate of nitrogen to the NV center is better in bulk diamond than in nanodiamond most likely due to surface effects limiting NV creation in NDs. On the other hand, nitrogen concentration measurements performed on detonation nanodiamonds agree well with values measured independently by EELS and highlight the higher nitrogen content in such NDs [16].

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