MPCVD Growth of ^{13}C -Enriched Diamond Single Crystals with Nitrogen Addition

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Abstract

This study describes the growth of ^{13}C -enriched (100)-oriented diamond single crystals by the MPCVD (microwave plasma chemical vapour deposition) process. All crystals are at least $6\times 6\text{mm}^2$ in area and 0.5-1.0mm in thickness. The samples with nominal ^{13}C percentages ($R = [^{13}\text{C}]/[^{13}\text{C}+^{12}\text{C}]$) of 0.011 (natural abundance), 0.10, 0.21, 0.24 and 0.34 were obtained by controlling the flow of the carbon-13 and carbon-12 methane feed gases. To obtain thicker and near-colourless quality ^{13}C -enriched diamond, 190ppm of nitrogen was added into the gas mixture. The shift towards lower frequency in the Raman peak positions and decrease in the thermal conductivities of the near-colourless crystals with increasing ^{13}C percentages are similar to the previous studies of isotopically-controlled diamond grown with no nitrogen additive. The images of the structural defects associated with ^{13}C -enrichment obtained by spatially-resolved X-ray rocking curve measurement show distinct patterned structures that are running parallel to the $\langle 100 \rangle$ direction. Moreover, the broadening in the line width of the nuclear magnetic resonance (NMR) peak from sp^3 ^{13}C correlates with increasing R . We also expand the study by injecting 500ppm of nitrogen. Higher nitrogen concentration leads to the formation of brown crystals. The brown crystals show far greater ^{13}C NMR peak intensity than the near-colourless. This suggests that paramagnetic nitrogen impurities in the brown crystals hasten the spin-lattice relaxation time of the ^{13}C nuclear spin that resulted in higher intensity. The isotopic splitting observed for the localized vibrational mode of the NVH^0 defect in brown crystals is attributed to the co-existence of both the ^{13}C (3114.2cm^{-1}) and ^{12}C (3123.5cm^{-1}). Unlike the isotopic splitting observed for NVH^0 defect, the peak position of the N_s^+ defect shifts towards lower frequency as R increases. Not only have we demonstrate the growth of bigger isotopically-controlled diamond single crystals, the results shown here has provided a framework to further investigate the interplay between ^{13}C atoms and nitrogen impurity.

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Introduction

The ability ^[1, 2] to grow isotopically engineered single crystals of diamonds has led to the emergence of new applications. For instance, control of the ¹³C composition, enables the ability to fine-tune the diamond band gap to fabricate multi-layered homojunction structures ^[3, 4]. The interaction between ¹³C nuclear spin and the electron spin of negatively charged nitrogen vacancy center (NV⁻) has also attracted widespread interests for quantum system development ^[5-7]. The shift of the first order Raman peak position from the isotopically-pure ¹³C diamond layer within diamond anvil cells has been exploited for the measurement of ultrahigh pressure in the diamond anvil ^[8]. The ¹³C concentration in CVD diamond modulates the thermal conductivity of diamond ^[9] significantly.

The isotopically-controlled diamonds shown in earlier studies were thin polycrystalline film and the single crystals are typically not big enough for a broad range of applications. Expanding the potential applications of isotopically-controlled diamond requires the availability of larger-sized material. Fortunately, the ability to manufacture larger-sized and thicker diamond single crystals of consistent quality is now possible given the recent advancement in CVD diamond growth technique ^[10-13].

In this work, we have successfully grown bigger ¹³C-enriched diamond single crystals ($>6.0 \times 6.0 \times 0.5 \text{ mm}^3$) by microwave plasma chemical vapour deposition (MPCVD). The ¹³C concentration investigated was 0.011 (natural abundance), 0.10, 21, 0.24, 0.34. It is of interests to explore the entire ¹³C concentration range and obtain isotopically pure ¹³C diamond. However, in order to produce thicker diamonds of near-colourless quality, we need considerable amount of ¹³CH₄ because of the prolonged deposition time. With the limited supply and the high costs of commercially-available ¹³CH₄, we have to limit the ¹³C concentration to 0.34. At nominal ¹³C percentage of 0.34, two ¹²CH₄ to one ¹³CH₄ are present in the feed gas. Although the crystals are not isotopically-pure, the properties of these larger specimens do not prohibit their practical use in the development of isotopically-engineered diamond systems. Note that all crystals appear near-colourless and have been grown with the

1 injection of minute amount of nitrogen. Injecting minute amount of nitrogen is a well-known
2 strategy to enhance the growth rate, much needed for a thick deposition, without compromise
3 of the crystal quality ^[11, 12]. The measured thermal conductivity, peak positions and line width
4 of the first order Raman mode of diamond are then compared with those presented in the
5 literature in order to assess the influence of the low amount of injected nitrogen. We then
6 map the lattice non-uniformity by spatially resolved X-Ray rocking curve measurement. The
7 line width broadening of the sp^3 ¹³C nuclear magnetic resonance (NMR) peak in relation to
8 the ¹³C concentration is also analysed.

9
10 We extended the study by introducing higher concentration of nitrogen. Injecting higher
11 concentration of nitrogen invariably led to the formation of brown diamond ^[14]. These brown
12 crystals only serve as platform to demonstrate the interaction between the nitrogen and the
13 ¹³C composition not a detailed study on the interplay between nitrogen and ¹³C concentration
14 on growth of diamond. From the NMR measurements, the brown crystals show about 10
15 times greater ¹³C NMR line intensity as compared to the near-colourless one. We finally
16 elaborate on the isotopic effects of two nitrogenous IR-active defects common to brown CVD
17 diamonds: neutral nitrogen-vacancy-hydrogen ^[15] (NVH⁰) and positive substitutional nitrogen
18 ^[16] (N_s⁺). More specifically, we will show that upon ¹³C-enrichment, the vibrational line due
19 to the NVH⁰ defect splits whereas the N_s⁺ line shifts towards lower frequency.

21 **Experimental**

22 All gases used in this work were at least 99.999% purity except ¹³CH₄, which is quoted at 99%
23 (Sigma Aldrich). The quoted isotopic purity was 99 atom % ¹³C. A pure nitrogen (N₂) gas
24 cylinder was used as the nitrogen precursor. Homoepitaxial diamond growth by MPCVD was
25 achieved using (100)-oriented type Iab or type Ib HPHT-grown diamond substrates. ¹³C
26 composition was controlled by the feed flow composition of ¹³CH₄ and ¹²CH₄:
27 (¹³CH₄)/(¹³CH₄+¹²CH₄), and denoted by **R** in the rest of the paper. Samples were deposited
28 with nominal **R** of 0.011 (natural abundance), 0.10, 0.21, 0.24 and 0.34.

1 The substrate temperature (T_s) was kept at $950\pm 25^\circ\text{C}$ and the deposition pressure was
2 maintained at 155Torr. The ratio of methane to hydrogen was 8 % and the microwave power
3 was 3000-3500W. Two nitrogen flow ratios were used: 190 ppm and 500 ppm (relative to
4 the total gas flow) to provide the near-colourless and brown crystals respectively. After
5 substrate removal and polishing, (100)-oriented diamond plate sizes with the average area of
6 $\sim 6\times 6\text{mm}^2$ and 0.5 to 1mm in thickness were obtained for characterization.

8 Micro-Raman spectra were collected by a Renishaw InVia Raman microscope employing
9 514.5nm Ar^+ laser excitation, in the backscattering geometry. The laser was focused down to
10 spot size of $\sim 1\text{-}2\mu\text{m}$, normal to the (100) plane of the diamond sample. All measurements
11 were recorded at room temperature. The reported Raman line widths were corrected by
12 subtracting the line width of the Rayleigh peak at 0cm^{-1} from the measured Raman line width.
13 Thermal conductivity measurements were determined by time-domain thermoreflectance
14 (TDTR) and 3ω techniques ^[17]. Fourier Transform (FT) infrared (IR) absorption spectra in
15 the spectral range of 2.5 to $25\mu\text{m}$ were recorded on a Nicolet 6700 spectrometer (Thermo
16 Scientific) using a KBR beam splitter and a DTGS KBr detector. Resolution of FTIR
17 spectrometer was 1.0cm^{-1} and a 4x beam condenser accessory was used. Selected pieces were
18 subsequently laser-diced into small cubes of approximately $0.8\times 0.8\times 0.8\text{mm}^3$ for NMR studies.
19 In all NMR measurements, the weight (0.0938g) of the samples was kept constant and was
20 loaded into a 4mm rotor tube for the ^{13}C magic-angle spinning (MAS) solid-state NMR
21 measurement using the Bruker Avance 400 at room temperature. Spectral width of the RF
22 radiation pulse is 30kHz. A delay cycle time of 30seconds and 128 scans were fixed.

24 **Results and Discussion**

25 Figure 1 shows that we have successfully produced near-colourless and brown ^{13}C -enriched
26 diamond single crystals ($> 6\times 6\times 0.5\text{mm}^3$). The input nitrogen concentration and growth rates
27 of the two crystal types are tabulated in Table 1. The crystal colour and growth rates have
28 been consistent in all deposition experiment of nominal **R**: 0.011 (natural abundance), 0.10,

1 0.21, 0.24 and 0.34. The near-colourless and brown crystals show $[N_s^+]$ of <0.3ppm and 0.8
 2 to 1.2 ppm respectively.

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 6 Figure 1. Photograph of the near-colourless (right) and brown diamond (left) produced with injected
 7 nitrogen concentration of 190ppm and 500ppm respectively.

8
 9 Table 1. Input nitrogen concentration, growth rates and positive substitutional nitrogen concentration
 10 ($[N_s^+]$) in the near-colourless and brown crystals.

	Near-colourless	Brown
Input nitrogen concentration (ppm)	190	500
Growth rates ($\mu\text{m/h}$)	16	19
$[N_s^+]$ (ppm)	<0.3	0.8-1.2

11
 12 After discussing the crystal appearance in relationship to the nitrogen feed concentration,
 13 determination of the ^{13}C percentage (**R**) is needed. The **R**-dependent behaviour of the first-
 14 order Raman frequency of diamond has been well-established ^[18-21]. Due to an increasing
 15 reduced mass, the Raman frequency naturally shifts to lower wavenumber. In fact, this
 16 relationship can be described using a non-linear equation derived by Volgelgesang et al ^[18].

$$Peak\ position\ (cm^{-1}) = 1332.82 - 34.77\mathbf{R} - 16.98\mathbf{R}^2$$

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2 We choose to rely on this polynomial relationship as the primary tool to determine **R** as the
3 reproducibility and reliability has been well-tested by Watanabe ^[1,2]. As shown in Figure 2a,
4 the experimental first order Raman frequency of diamond agrees with the results of reference
5 18. Figure 2b illustrates the dependence of the peak position as a function of **R**. The
6 favourable match between the peak positions and existing theory strongly supports the high
7 reproducibility of verifying **R** using Raman spectroscopy.

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3 Figure 2. (a) Raman spectra of the isotopically-controlled diamond single crystals. (b) Comparison of
 4 the first order Raman frequency of diamond between the material of this work ($\bullet$) and Reference 18 (—)
 5 —). The error bars of the Raman frequency are smaller than the size of the data points.

1 Figure 3 shows the observed first order Raman line width after subtracting the laser line
2 width of $\sim 2.0\text{cm}^{-1}$. As illustrated in Figure 3, the line width broadens non-linearly with
3 increasing ^{13}C percentage (**R**). This broadening is clearly a result of the isotopic disorder [22].
4 Although the broadening behaviour in Figure 3 follows that of many others [20, 21, 23-25], the
5 reported line width varies significantly. We also present a distinct set of line widths, which
6 surprisingly, is the narrowest thus far. But, direct comparison of the observed line width may
7 not be fruitful due to system resolution of the Raman system.

8

9 On the contrary, the different increase in the line width per unit **R** is worthy of comparison
10 since systematic errors between different instruments are largely eliminated. To illustrate this
11 point, the reported line widths from Anthony and Banholzer [23, 24] have been added in Figure
12 3. We have chosen to use the ^{13}C -enriched HPHT-grown crystals reported by them for
13 comparison because of the high crystal quality and the comparable sample size of $\sim 2.5\text{mm}$
14 ($\geq 6\text{mm}$ in this study). A careful inspection of Figure 3 illustrates the relatively gentle rise in
15 the line width of the CVD crystals in this work. This observation requires further study.

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Figure 3. Comparison of the first order Raman line width of diamond between the ^{13}C CVD diamond of this work and the HPHT-grown crystals shown in References 23 & 24.

To eliminate the possibility that the Raman line width broadening is due to crystalline defects (i.e. strain in the crystal) resulting from faster growth, thermal conductivity (TC) measurement were carried out to shed light about the influence of the 190ppm of injected nitrogen concentration. Besides, the isotope-modulated TC is one of the more technologically important aspect of isotope-controlled diamond for heat-spreader applications. Figure 4 shows the measured TC as a function of ^{13}C percentage ($\mathbf{R}$). As shown by the fitted trend line in Figure 4, TC weakens exponentially with increasing $\mathbf{R}$, which agrees well with existing experimental results and theory ^[9, 26-29]. This behaviour can be explained and modelled by phonon scattering processes. When using diamond crystal as a heat-transfer medium, heat energy is kinetically-transported via collective lattice vibrations, termed phonons. Increased mixing ratio between ^{13}C and ^{12}C elevates anharmonicity in the lattice. This anharmonicity dissipates the collective lattice vibrations, or scatters the phonons, so to speak. The overall outcome is a reduction in efficiency of heat transfer.

1 The consistency in the measured TC values to the published reports without nitrogen strongly
 2 supports that the line width broadening and the peak shift of first order Raman mode is not
 3 due to the presence of low nitrogen amount in the lattice but that of the ^{13}C -enrichment.

4
 5 Figure 4. Plot of measured thermal conductivity (W/m.K) as a function of **R**. Measurements limited to
 6 near-colourless crystals.

7

8 In order to visualize ^[30] the anharmonicity of the lattice as observed from Raman
 9 spectroscopy and thermal conductivity measurements, we performed spatially resolved X-ray
 10 rocking curve measurement. Figure 5a and b show the spatially resolved X-ray rocking curve
 11 measurement at the (220) plane for crystals of **R**=0.10 and **R**=0.24 respectively. The
 12 measured region corresponds to approximately 5x5mm² of the samples. In both maps, the
 13 variation in the full-width-at-half-maxima (FWHM) of the X-ray rocking curve is represented
 14 by a coloured scale bar ranging between 0 and 100 micro radian (μRad).

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Figure 5. The X-ray section topography image at the (220) plane of ^{13}C -enriched samples with $R=0.10$ (a) and $R=0.24$ (b) respectively.

The histograms in Figure 6 correspond to the X-ray rocking curve FWHM maps in Figure 5. It is apparent that the ^{13}C -enriched sample of $R=0.24$ shows a higher average FWHM ($45\mu\text{Rad}$) compared to that of $R=0.10$ ($40\mu\text{Rad}$). The former also shows relatively broader distribution in the FWHM values that are also more skewed towards the higher FWHM range.

One other striking similarity between Figure 5a and b is the clear presence of distinct patterned structures running diagonally, at roughly 45° of the map, along the <100> plane of the samples. These diagonally aligned strips clearly are of a higher local FWHM. Although these patterns can possibly be attributable to structural defects that originate from surface/sub-surface damage of the substrate^[31], it is surprising that they are able to cover the entire sample. More work is underway to fully understand the effect of ¹³C incorporation on the lattice non-uniformity.

Figure 6. Histograms of the X-ray rocking curve FWHM measured for the ¹³C-enriched ($R = 0.10$ and 0.24) in Figure 5.

NMR spectroscopy on ¹³C can potentially distinguish^[32] whether the Raman broadening is due to the reasons other than the ¹³C percentage (R). Figure 7a shows the ¹³C MAS NMR spectra normalized to the sp^3 ¹³C peak centering at ~35ppm. The most striking observation is that the NMR line width broadens linearly with R as depicted in Figure 7b.

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4 Figure 7. (a) ^{13}C MAS-NMR spectra of ^{13}C -enriched diamond single crystals when reduced to tiny
 5 grits of $\sim 0.8 \times 0.8 \times 0.8 \text{ mm}^3$. (b) Plot of NMR line width (Hz) as a function of ^{13}C percentage (R).

1

2 The commonality between a nuclear spin-flip transition and inelastic scattering mechanisms
 3 are non-intuitive at first. However, a correlation between the NMR line width and the first
 4 order Raman line width of diamond shown in Figure 8 implies that the line width broadening
 5 shares an underlying origin in the isotopic disorder. Similar observation have been obtained
 6 in NMR study of ultrapure ^{73}Ge -enriched single crystals ^[33]. The authors have concluded that
 7 the contribution to the NMR line width scales linearly with the concentration of magnetic
 8 ^{73}Ge nuclei.

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10 Figure 8. Plot of the first order Raman line width (cm⁻¹) as a function of NMR line width (Hz).

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2 After establishing that small amount (190ppm) of nitrogen does not drastically alter the
3 properties of ^{13}C enriched near-colourless crystals, we extended the study by testing higher
4 (500ppm) concentration of nitrogen. Injecting higher concentration of nitrogen invariably led
5 to the formation of brown diamond ^[14]. We found that the brown share identical first order
6 Raman characteristics (see Figures 2 and 3) to that of the near-colourless samples. Despite
7 rendering a brown colouration ^[34], the amount of nitrogen present in the brown crystals
8 apparently does not affect the phonon properties at all.

9

10 In contrast to the NMR line width, which broadens monotonically as a function of the ^{13}C
11 percentage (**R**), we found no direct correlation between **R** and peak intensities. For example,
12 Figure 9 compares the sp^3 ^{13}C NMR peak of a near-colourless sample (**R**=0.21) and a brown
13 sample (**R**=0.24) plotted on an identical y-scale range, without data treatment. Despite the
14 0.03 difference in **R**, the NMR intensity of the brown sample (**R**=0.24) exceeds that of the
15 near-colourless sample (**R**=0.21) by about 10 times, suggesting that the nitrogen impurity
16 concentration plays a major role in the NMR intensity. This disparity in NMR intensity has
17 initially been difficult to explain considering that we fixed sampling volume (4mm rotor),
18 sample size ($\sim 0.8 \times 0.8 \times 0.8 \text{ mm}^3$), mass (0.0938g) of diamond grits, delay cycle time of 30s
19 and number of accumulated scans to 128 during solid-state NMR experiment.

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21 It has been reported^[35-37] that pure diamond exhibits an extended nuclear spin-lattice
22 relaxation time (T_1) of the ^{13}C nuclei whereas any nitrogen present shortens it. It is known
23 that nitrogen (paramagnetic) hastens T_1 due to a cooperative dipolar interactions ^[35] between
24 the ^{13}C nuclear spin and the electron spin of paramagnetic species. By extending this concept
25 to the example shown in Figure 9, the exceptionally high NMR intensity from the brown
26 diamond can likely be explained by the relatively faster relaxation of the ^{13}C nuclei spin from
27 the higher-energy to lower-energy spin state. In this case, majority of the ^{13}C nuclear spin
28 population occupies the lower energy state at any instance. These ^{13}C nuclear spin population
29 occupying the lower energy state can readily absorb the incident radiation and undergo a

1 “spin-flip” transition to the higher energy level, which leads to rapid accumulation of NMR
2 intensity.

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5 Figure 9. ^{13}C MAS-NMR spectra of one near-colourless sample ($R=0.21$) and another brown sample
6 ($R=0.24$). Take note of the drastic difference in the NMR intensities. The brown and near-colourless
7 samples correspond to the ones shown in Figure 1.

8

9 One of the approaches to look at the influence of nitrogen on ^{13}C -enriched crystals is to
10 characterize the nitrogenous IR-active defects such as NVH^0 and N_s^+ that are commonly seen
11 on brown CVD diamond. This is because the atomic arrangement of NVH^0 and N_s^+ involves
12 direct or indirect chemical bonding to the sp^3 carbon lattice. Hence, isotopic effect due to ^{13}C
13 enrichment is expected.

14

15 Brown CVD diamond of the natural isotopic abundance ($R=0.011$) shows distinct NVH^0
16 vibration centering at 3123.5cm^{-1} . Upon ^{13}C enrichment, this vibrational line splits to give an
17 additional peak at 3114.24cm^{-1} as exemplified in Figure 10a. Figure 10b shows the widely-

1 accepted structure of the NVH⁰ unit. In the NVH⁰ unit, a C-H vibration in the immediate
2 vicinity of a vacancy sited next to a substitutional nitrogen atom has been determined ^[15] to
3 be origin of the 3123.5cm⁻¹ vibration. Due to the involvement of a single localized C-H
4 vibration, the observed isotopic splitting of the NVH⁰ vibration can be attributed to the co-
5 existence of both the ¹³C (3114.24cm⁻¹) and ¹²C (3123.5cm⁻¹) analogues of the NVH⁰ defect,
6 consistent with observation made by Fuchs et al ^[38] earlier in 1995 on polycrystalline films.
7 By systematic control of **R** at 0.011, 0.50 and 1.00, Fuchs and co-workers have brilliantly
8 concluded that no nitrogen is involved and hydrogen is bonded to only one carbon, which
9 largely agrees with the structure shown in Figure 10b.

10
11 In this work, we expand upon the contributions of Fuchs et al by using relatively smaller
12 increment of **R** (0.011, 0.10, 0.21, 0.24 and 0.34) and study the isotopic splitting ratios of the
13 3114.24cm⁻¹ and 3123.5cm⁻¹ lines of the NVH⁰ defect.

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Figure 10. (a) Isotopic splitting of the NVH⁰ vibrational line due to the co-existence of the ¹³C analogue (3114.24cm⁻¹) and ¹²C analogue (3123.5cm⁻¹). (b) Corresponding structure of the NVH⁰ defect.

After introducing a linear base line, the isotopic NVH⁰ split can be quantified based on the intensity ratio of the 3114.24cm⁻¹ to 3123.5cm⁻¹ vibrational line: I_{C13}/I_{C12} . As summarized in

1 Table 2, I_{C13}/I_{C12} agrees well with the corresponding input flow ratio of $^{13}\text{CH}_4$ to $^{12}\text{CH}_4$. The
 2 reasonable match between input flow ratio of $^{13}\text{CH}_4$ to $^{12}\text{CH}_4$ and I_{C13}/I_{C12} substantiates the
 3 absence of isotopic effect in NVH^0 formation. This isotopic splitting ratio of the NVH^0
 4 vibration can possibly be used as an internal marker of the ^{13}C composition, but this method
 5 is restricted by the detection limit of the 3114.24cm^{-1} line.

6

7 Table 2. Comparison between I_{C13}/I_{C12} and the corresponding feed flow ratios of $^{13}\text{CH}_4$ to $^{12}\text{CH}_4$

R	Approximate Flow Ratios of $^{13}\text{CH}_4$ to $^{12}\text{CH}_4$	(I_{C13}/I_{C12})
0.10	0.10	0.12 ± 0.03
0.20	0.25	0.23 ± 0.04
0.24	0.30	0.30 ± 0.01
0.34	0.50	0.49 ± 0.02

8

9 The next common IR-active defect in brown CVD diamond of natural isotopic abundance is
 10 the positively-charged substitutional nitrogen: N_s^+ , centering at 1332.0cm^{-1} . Unlike the
 11 isotopic splitting observed for the localized vibrational mode of the NVH^0 defect, the peak
 12 position of the N_s^+ defect shifts towards lower frequency as a function of **R** (Figure 11a).
 13 Figure 11b tracks the N_s^+ peak position as a function of **R**. This shift can be rationalized by
 14 the fact that the N_s^+ atom is substitutional ^[16], as such it is covalently-bonded to four other
 15 carbons in diamond lattice, thereby a “phonon-type” vibration.

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3 Figure 11. (a) The N_s^+ vibrational line shifts from 1332 cm^{-1} to 1322.98 cm^{-1} when R increases from
4 0.011 to 0.24. (b) Peak position of N_s^+ vibration as a function of R .

5

1 Summary

2 We demonstrate the ability to manufacture bigger ($\geq 6 \times 6 \times 0.5 \text{ mm}^3$) isotopically-controlled
3 diamond single crystals (**R** of 0.011, 0.10, 0.21, 0.24 and 0.34) of consistent quality. The
4 average growth rate of the near-colourless crystals is $16 \mu\text{m/h}$, based on an input nitrogen
5 concentration of 190ppm. Compared to ^{13}C diamond grown with no nitrogen, the larger-sized
6 isotopically-controlled crystals here are similar in terms of the shift in the peak position and
7 broadening of the line width of the first order Raman line. In the range of the **R** investigated,
8 the measured thermal conductivity weakens exponentially as such: $\text{TC (W/m.K)} = 563 \text{ R}^{-0.283}$,
9 which also agrees well with others. To a first approximation, the Raman and thermal
10 conductivity studies suggest that the variation in the phonon properties have been dominated
11 by isotopic effects, that greatly outweighs that originating from the 190ppm of injected
12 nitrogen.

13
14 Spatially resolved X-ray rocking curve maps are then presented at the (220) plane for sample
15 of **R**=0.10 and another of **R**=0.24. A greater lattice distortion of the latter is clear from the
16 relatively broader FWHM maps, which could be attributable to the higher ^{13}C composition.
17 We also observe bands of higher local FWHM directed along the $\langle 100 \rangle$ direction of the
18 samples. The strange fact that these bands can cover the entire measurement area of $5 \times 5 \text{ mm}^2$
19 implies that it may not be simply due to “grown-in” structural imperfection of the
20 homoepitaxial growth. Lastly, the $\text{sp}^3 \text{ }^{13}\text{C}$ NMR spectra have been found to broaden linearly
21 as a function of **R**: $\text{NMR Line Width (Hz)} = 507.31 \text{ R} + 119.59$. Similar behaviour has been
22 also observed in high-purity ^{73}Ge -enriched single crystal.

23
24 In attempt to demonstrate the interaction between the nitrogen and the ^{13}C composition as a
25 preliminary study, we have tested 500ppm of nitrogen. This concentration of nitrogen
26 consistently provides brown-coloured crystals. From the NMR measurements, we observed
27 that the brown crystals show about 10 times greater ^{13}C NMR line intensity as compared to
28 the near-colourless one. We explained this observation based on the rule that the
29 paramagnetic nitrogen impurities hasten the spin-lattice relaxation time of the ^{13}C nuclear

spin. Isotopic effects of two IR-active nitrogenous defects common to brown CVD diamond are successfully evaluated. We found that NVH⁰ vibration at 3123.5cm⁻¹ splits to give another line at 3114.24cm⁻¹ upon ¹³C-enrichment. The 3123.5cm⁻¹ line corresponds to the ¹²C analogue of the defect whereas the 3114.24cm⁻¹ line is due to the ¹³C analogue. Quantification of the splitting ratios supports the absence of kinetic isotope effect in the formation of NVH⁰. We describe the **R**-dependent shift of the N_S⁺ peak position as: Peak position (cm⁻¹) = 1332.5 – 38.8**R**. Although both isotopic splitting ratio of the NVH⁰ vibration and peak position of the N_S⁺ line can possibly be used as an internal marker of the ¹³C composition, such a method is only restricted to brown CVD diamond of significant nitrogen concentration.

Not only have we demonstrated the growth of larger isotopically controlled diamond, the body of results shown here has provided a framework to further investigate the interplay between ¹³C atoms and nitrogen impurity. We envision that more novel uses and designs of isotopically engineered diamond platforms to be uncovered in future.

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