LETTER TO THE EDITOR

Nitrogen incorporation in diamond films homoepitaxially grown by chemical vapour deposition

Konstantin Iakoubovskii†, Guy J Adriaenssens† and Yogesh K Vohra‡

† Laboratorium voor Halfgeleiderfysica, K U Leuven, Celestijnenlaan 200 D,
B-3001 Heverlee-Leuven, Belgium
‡ Department of Physics, University of Alabama at Birmingham, Birmingham, AL 35294-1170, USA

E-mail: `kostya.iakoubovskii@fys.kuleuven.ac.be`

Abstract. Photoluminescence, optical absorption and electron spin-resonance results are reported for diamond films homoepitaxially grown by chemical vapour deposition on $\langle 100 \rangle$-oriented natural IIa diamond. Measured dependencies of the corresponding signals on the growth temperature in the range 950–2100 °C suggest that while most of the nitrogen is present in our films as single atoms, a small part (about 10^{-3} of all of the nitrogen) could be incorporated as N_2 molecules.

It is widely believed that nitrogen is a dominant impurity in diamond, which strongly affects its optical, electrical and mechanical properties. Several tens of nitrogen-related defect centres are known (Baker and Newton 1995, Davies 1999). Most of them are present in trace amounts (parts per million, ppm, and lower), but the concentration of three centres, called A, B and C (or P1), can be as high as 0.3 per cent (Kanda *et al* 1999). The C and A centres are known to be a single substitutional nitrogen atom and a nearest-neighbour pair of substitutional nitrogen atoms, respectively; the B complex is believed to consist of four substitutional nitrogen atoms in a tetrahedral coordination around a vacancy (Davies 1999). Laboratory experiments and investigation of natural diamonds show that high-pressure high-temperature (HPHT) annealing results in aggregation of nitrogen from the C to the A and then to the B form. In this letter the behaviour of these centres in CVD diamond is examined. While the concentration of the C centres can be accurately determined by electron spin resonance (ESR), the A and B complexes can only be detected by IR or UV absorption with a sensitivity not better than 1 ppm. None of these centres is luminescent. A, B and C nitrogen effectively capture vacancies forming N–V–N, 4N–2V and N–V complexes, respectively (Davies 1999). The trapping efficiencies for the A and C centres are about 1.7 and 35 times higher than for the B centres, respectively (Davies 1999). All the above nitrogen–vacancy complexes produce narrow zero-phonon lines (ZPLs) in optical absorption and photoluminescence (PL) and therefore can be detected with a high sensitivity (at the parts per billion level). Several optical centres with corresponding ZPLs were attributed (Davies 1999, Iakoubovskii and Adriaenssens 2000a) to the different charge states of nitrogen–vacancy complexes: $[N–V]^-$ (with the ZPL at 1.945 eV), $[N–V]^0$ (2.156 eV), $[N–V–N]^-$ or H2 (1.267 eV), $[N–V–N]^0$ or H3 (2.463 eV), $[4N–2V]^0$ or H4 (2.499 eV).

Unlike optical absorption, PL intensity depends not only on the concentration of occupied centres, but also on the lifetimes of their excited states. The latter are affected by many factors, like stress, presence of other impurities etc. These may lead to the broadening of PL lines and

hamper determination of absolute concentrations from PL measurements (Iakoubovskii *et al* 1999, Iakoubovskii and Adriaenssens 2000b). However, by analysing the *relative* strength of PL intensity from different nitrogen–vacancy complexes, qualitative information on the nitrogen aggregation can be deduced. While this method gives consistent results for irradiated diamond (Davies 1999), it does not work for as-grown HPHT crystals: although they contain nitrogen predominantly in the C form, the PL is dominated by the N–V–N rather than N–V lines, with the N–V–N emission being restricted to the $\langle 100 \rangle$ sectors (Fish *et al* 1999). A possible explanation was given by Dodge (1986): during the HPHT synthesis, nitrogen is dissolved in graphite and/or in metal catalyst as single atoms and therefore incorporates in growing diamond also as single atoms. At the high temperature of the synthesis (1200–1800 °C) there is a probability that two nitrogen atoms migrate to each other forming a nearest-neighbour pair. If this happens in the $\langle 100 \rangle$ plane, the next atomic layer should contain a vacancy in order to preserve the continuity of growth, thus forming an N–V–N centre.

Similar to HPHT crystals, diamond films grown by the chemical vapour deposition (CVD) technique contain nitrogen exclusively in the C form. However, while the concentration of optically active nitrogen in HPHT diamond is typically 200–500 ppm and can reach 1900 ppm (Kanda *et al* 1999), it usually does not exceed 50 ppm in CVD films (Iakoubovskii *et al* 1999, Iakoubovskii and Adriaenssens 2000c, Rohrer *et al* 1996a, b). N_2 gas is commonly used for nitrogen doping of CVD diamond. In this case, nitrogen incorporation efficiency, which is determined as the nitrogen-to-carbon ratio in the film normalized to the N/C ratio in the gas phase, is about 10^{-4} (Bergmaier *et al* 1996, Eccles *et al* 1999, Leeds *et al* 1999, Rohrer *et al* 1996a, b). However, the incorporation efficiency can be close to unity if a dopant source with weakly bonded nitrogen, e.g., NH_3, is used (Edgar *et al* 1998). This result can be understood if nitrogen preferentially incorporates as single atoms, but their concentration is low in the N_2-containing CVD plasma. Indeed, direct mass-spectroscopic investigations show that there is almost no N_2 dissociation at the typical conditions of hot-filament or microwave-assisted CVD synthesis (Leeds *et al* 1999). Most CVD films are nominally undoped, but they do contain nitrogen. This is believed to be due to atmospheric N_2 contamination. Thus, typical CVD plasma contains relatively few nitrogen atoms having relatively high incorporation ability and a lot of N_2 molecules. Questions arise as to whether these molecules can incorporate into the growing film and how efficient this incorporation can be, which will be the major topic of this letter.

Several groups have reported on the detection of the N–V–N centres in CVD films by PL (Doverspike *et al* 1993, Lin *et al* 1996, Snail *et al* 1992). Two possibilities for the N–V–N complex formation should be considered: aggregation of single nitrogen atoms and N_2 incorporation, followed by capture of a vacancy. It is widely believed that nitrogen aggregation is extremely inefficient in CVD diamond because of the low growth temperatures (typically 700–1000 °C). However, the observed N–V–N luminescence intensity was also weak and the possibility of aggregation could not be excluded. While the nitrogen aggregation has a strong temperature dependence with an activation energy of about 6 eV for cubic sectors (Taylor *et al* 1996), the temperature dependence of N_2 incorporation is expected to be much weaker. In order to test these two possibilities, CVD diamond films were grown in the wide temperature range of 950 to 2100 °C. To increase the concentration of the N–V–N centres, films were synthesized homoepitaxially on the $\langle 100 \rangle$-oriented IIa natural diamond crystals and therefore had predominantly $\langle 100 \rangle$ growth sectors.

The growth procedure and some results on sample characterization, in particular ESR measurements, are described in detail in our previous paper (Yan and Vohra 1999) and just some key points will be discussed here. Films were grown from the CH_4/H_2 gas mixture by microwave-assisted CVD in a stainless steel reactor. The deposition parameters were: CH_4

content 1–6%, microwave power 500–1200 W, reactor pressure 60–200 Torr, gas flow rate 500 cm^3 min^{-1}. Substrate temperature was controlled by a two-colour infrared pyrometer. The contribution of the plasma emission to the pyrometer reading was carefully checked and taken into account. Moreover, consistent results were obtained when this pyrometer was used to measure the temperature of the nitrogen aggregation process in diamond (Iakoubovskii *et al* 2000a). During the deposition the plasma was touching the substrate, which had to be cooled in order to maintain the desired temperature. This resulted in extensive ion bombardment of the surface and could be partially responsible for the high growth rates achieved (up to 30 μm h^{-1}). Optical emission spectra from our CVD plasma show high concentrations of H$_\alpha$, C$_2$ and CN radicals indicating residual nitrogen present in the chamber even though nitrogen is not intentionally added to the gas mixture. The main reason for the nitrogen contamination is probably insufficient vacuum (0.1 Torr) in the CVD reactor prior to deposition

PL spectra were recorded with a confocal micro-Raman spectrometer at 77 and 300 K under 2.41, 2.54 or 2.71 eV excitation provided by a CW Ar$^+$ laser. Utilization of a confocal mode allowed detection of PL from a volume not larger than $2 \times 2 \times 6$ μm^3. Since the film thickness was in the range 100–300 μm, no substrate contribution could be present, as was nevertheless confirmed by independent measurements. Several sample spots have been scanned and no strong variation in the spectral shape and intensity was observed. Identification of PL centres was carried out by analysing the position and relative intensities of corresponding ZPLs and vibronic bands recorded for different excitation energies at different temperatures. The dimensionless integrated ratio of the ZPL to the diamond Raman peak was used as a measure of PL intensity from a certain optical centre. Absorption spectra were recorded in the range 0.12–5.6 eV at room temperature using commercial FTIR and home-built spectrometers.

Figure 1 presents a typical room-temperature PL spectrum recorded under 2.71 eV excitation from a film grown at 1300 °C. The spectrum is dominated by the [N–V–N]^0 system with a small contribution of the [N–V]^0, [N–V]$^-$ and TR12$'$ centres. The latter is a recently characterized interstitial-related centre with a vibronic structure very similar to that of the radiation-induced TR12 centre (Iakoubovskii and Adriaenssens 2000b). The UV and
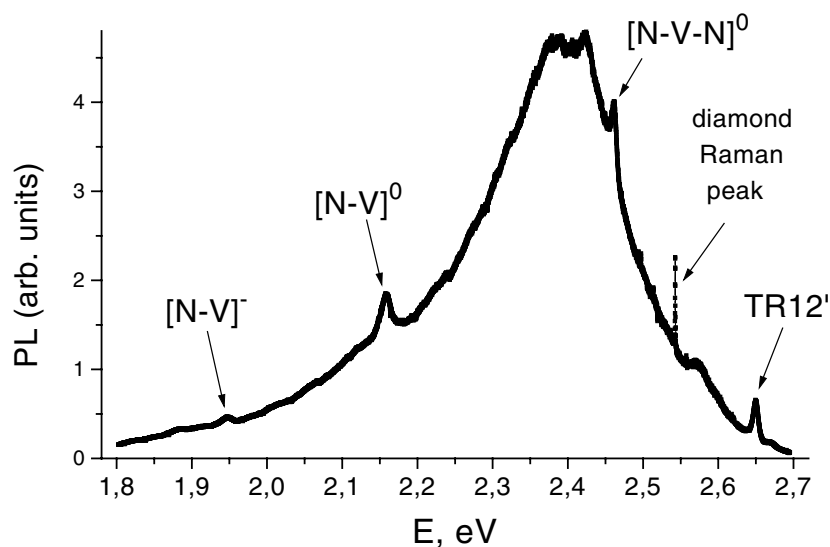

Figure 1. Room-temperature PL spectrum recorded under 2.71 eV excitation from a film grown at 1300 °C.

IR absorption spectra were dominated by the absorption from the C centre with a small or negligible contribution from the A nitrogen. Spectra were distorted by the scattering and absorption from the substrate and non-diamond carbon present in some parts of the sample. Consequently, no attempt at their accurate analysis was made and therefore the spectra are not shown. A sharp absorption peak at 0.913 eV was observed for all samples. Isotopic substitution study (Fuchs *et al* 1995) unambiguously assigned this line to an electronic transition at a hydrogen-related defect centre. The absorption from the observed PL centres was less than 10^{-2}, which sets an upper limit on their concentration of about 1 ppm (Davies 1999). Thus, the single substitutional centre was a dominant form of nitrogen in our samples.

The observed strength of PL from the $[N–V–N]^0$ centre is unusually high for CVD diamond, but rather typical for $\langle 100 \rangle$ sectors of commercial HPHT crystals. This fact can be understood by recalling that most CVD samples grown in other reactors are unoriented polycrystalline films with abundant non-$\langle 100 \rangle$ sectors, which is unfavourable for N–V–N formation. Moreover, the aggressive character of the deposition in our system could enhance the nitrogen incorporation rate. Indeed, a concentration of C centres as high as 100 ppm was observed in our nominally undoped films (Yan and Vohra 1999). In order to reveal the origin of the N–V–N defects in our samples, the dependence of the PL intensity on the growth temperature was investigated and the results are summarized in figure 2.

No variation in the width of the diamond Raman peak and the PL and absorption lines with growth temperature was observed, and therefore no difference in the stress or lifetimes of excited states of different centres in various samples should be expected. As we have demonstrated previously (Iakoubovskii and Adriaenssens 2000a, c), care should be taken when determining relative concentrations of defect centres from ESR or optical measurements: variations in the Fermi level position can induce strong changes in the corresponding signals. In order to monitor such changes, a ratio of the PL from different charge states of the N–V centre was plotted in figure 2(a). This ratio is sensitive to the Fermi level shift (Iakoubovskii and Adriaenssens 2000a). It is remarkably stable for all samples studied, which facilitates the analysis of the PL and ESR results. Therefore, only the curves for one (neutral) charge state of the N–V and N–V–N centres are presented in figure 2(a). They both show maxima around 1300 °C with a decrease at high and low temperatures. In order to reproduce the low-temperature results, several samples were grown at similar conditions in another CVD reactor in the temperature range 800–1500 °C. Results obtained on those samples showed a similar temperature trend, but different absolute values, and therefore are not plotted in figure 2.

The temperature behaviour shown in figure 2(a) is probably caused by changes in the overall nitrogen incorporation due to the variations in the plasma chemistry. In order to compensate for these changes, the $[N–V–N]^0$ curve is shown normalized to the $[N–V]^0$ curve and to the concentration of the C centres in figure 2(b). Both normalizations reveal a similar slow decrease in the $[N–V–N]^0$ content with growth temperature. This result excludes the possibility of nitrogen aggregation being the mechanism of formation of the N–V–N centres in our samples and leaves N_2 incorporation as the likely mechanism of the N–V–N generation. The observed decrease in normalized N–V–N PL intensity with temperature can then be naturally explained: in order to increase the substrate temperature in our system, the microwave power had to be increased. This could lead to a higher N_2 dissociation rate and therefore smaller N_2 concentration in the plasma.

Furthermore, a direct check for possible nitrogen aggregation was performed. Several $\langle 100 \rangle$-oriented HPHT diamond samples with nitrogen content (50–200 ppm) and size ($2 \times 2 \times 0.5$ mm^3) very close to those for the CVD samples were annealed in the same system as was used for CVD depositions, with and without CH_4 gas added. Nitrogen aggregation was monitored by IR absorption before and after annealing. No aggregation of single nitrogen to
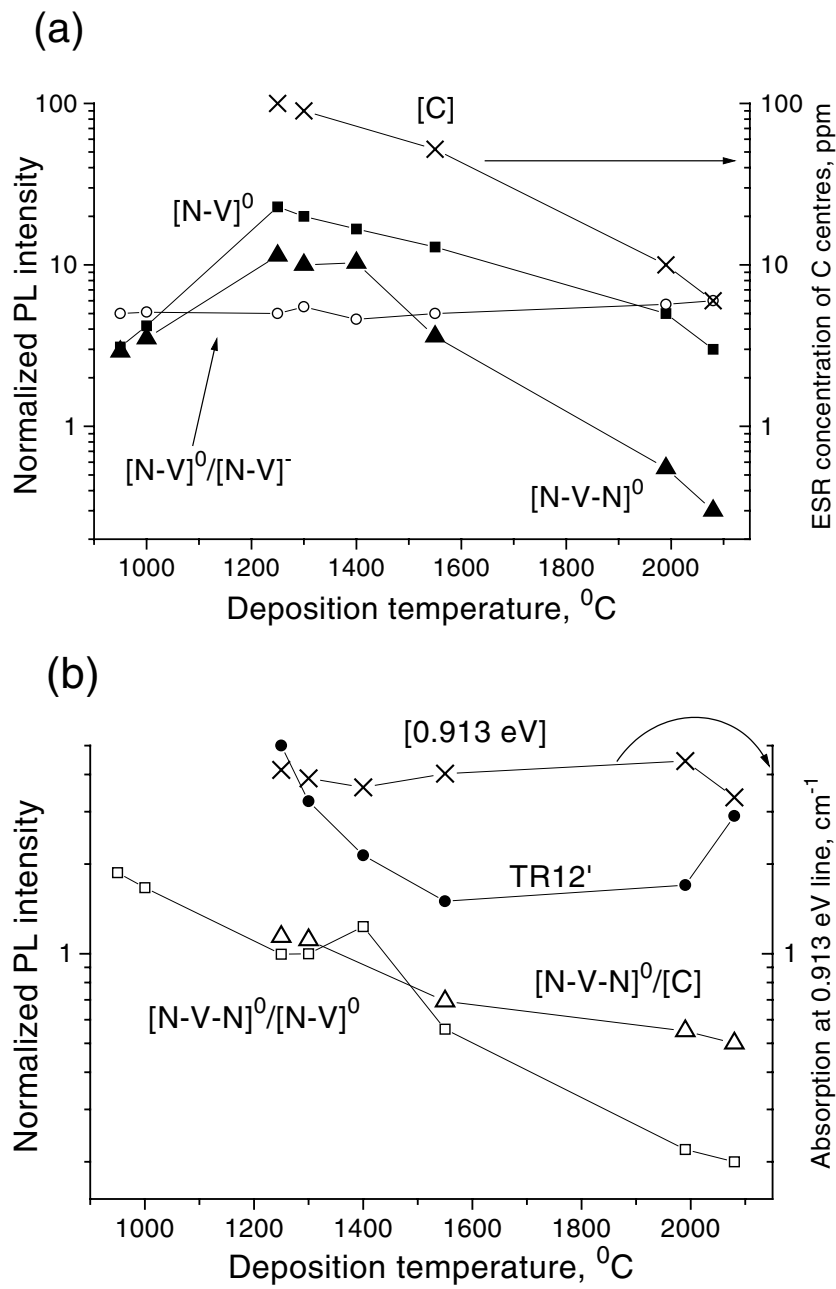
(a)

(b)

Figure 2. Dependencies on the growth temperature of the intensity of the PL (excited at 2.71 eV) and absorption signals for homoepitaxial CVD diamond (full symbols); ratios of these are also included (open symbols). In (a), also shown is the concentration of the C centres as determined by ESR (Yan and Vohra 1999).

pairs ($<5\%$) was observed after annealing in the temperature range 1000–1700 °C.

In order to estimate the maximum concentration of the $[N–V–N]^0$ centres in our samples, PL was measured under the same conditions for the sample grown at 1250 °C and for a

natural diamond where the $[N–V–N]^0$ concentration was determined by optical absorption using the calibration of Davies (1999). A value of 0.1 ppm was deduced, in agreement with our absorption measurements.

Also shown in figure 2(b) are the PL from the TR12′ and the absorption from the 0.913 eV centres. Our previous measurements on heteroepitaxial CVD films (Iakoubovskii *et al* 2000b) showed that these centres were absent if no nitrogen-related centres could be detected, and appeared with nitrogen doping. However, the other results in figure 2 demonstrate that the intensities of the PL and absorption from these centres do not follow the nitrogen content. While in the films used for figure 2 the Fermi level position is almost constant, it was certainly moved up by nitrogen doping in the heteroepitaxial samples, leading to changes in the occupations of many defect centres (Iakoubovskii and Adriaenssens 2000c). This result may be considered an example of a possible false identification of a 'nitrogen-related' defect.

References

Baker J M and Newton M E 1995 *Appl. Magn. Reson.* **8** 207
Bergmaier A, Dollinger G, Faestermann T, Frey C M, Ferguson M, Guttler H, Schultz G and Willerscheid H 1996 *Diamond Relat. Mater.* **5** 995
Davies G 1999 *Physica* B **273+274** 15
Dodge C N 1986 *PhD Thesis* University of Reading, UK
Doverspike K, Butler J E and Freitas J A Jr 1993 *Diamond Relat. Mater.* **2** 1078
Eccles A J, Steele T A, Afzal A, Rego C A, Ahmed W, May P W and Leeds S M 1999 *Thin Solid Films* **343+344** 627
Edgar J H, Xie Z Y and Braski D N 1998 *Diamond Relat. Mater.* **7** 35
Fish M L, Massler O, Reid J A, MacGregor R and Commins J D 1999 *Diamond Relat. Mater.* **8** 1511
Fuchs F, Wild C, Schwarz K and Koidl P 1995 *Diamond Relat. Mater.* **4** 652
Iakoubovskii K and Adriaenssens G J 2000a *J. Phys.: Condens. Matter* **12** 189
Iakoubovskii K and Adriaenssens G J 2000b *Phys. Status Solidi* a at press
Iakoubovskii K and Adriaenssens G J 2000c *Diamond Relat. Mater.* **9** 1349
Iakoubovskii K, Adriaenssens G J and Vohra Y K 2000a to be published
Iakoubovskii K, Adriaenssens G J and Vohra Y K 2000b unpublished
Iakoubovskii K, Stesmans A, Adriaenssens G J, Provoost R, Silverans R E and Raiko V 1999 *Phys. Status Solidi* a **174** 137
Kanda H, Akaishi M and Yamaoka Sh 1999 *Diamond Relat. Mater.* **8** 1441
Leeds S M, May P W, Ashfold M N R and Rosser K N 1999 *Diamond Relat. Mater.* **8** 226
Lin L T S, Popovici G, Mori Y, Hiraki A, Prelas M A, Spitsyn B V, Khasawinah S and Sung T 1996 *Diamond Relat. Mater.* **5** 1236
Rohrer E, Graeff C F O, Jansen R, Nebel C E, Stutzman M, Guttler H and Zachai R 1996a *Phys. Rev.* B **54** 7874
Rohrer E, Graeff C F O, Jansen R, Nebel C E, Stutzman M, Guttler H and Zachai R 1996b *Appl. Phys. Lett.* **69** 3215
Snail K A, Vold C L, Marks C M and Freitas J A Jr 1992 *Diamond Relat. Mater.* **1** 180
Taylor W R, Canil D and Milledge H J 1996 *Geochim. Cosmochim. Acta* **60** 4725
Yan Ch and Vohra Y K 1999 *Diamond Relat. Mater.* **8** 2022