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2004 J. Phys.: Condens. Matter 16 6897

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Alignment of Ni- and Co-related centres during the growth of high-pressure–high-temperature diamond

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Received 25 June 2004, in final form 23 August 2004

Published 17 September 2004

Online at stacks.iop.org/JPhysCM/16/6897

doi:10.1088/0953-8984/16/39/022

Abstract

An extensive study of Co- and Ni-related centres in high-pressure synthetic diamond, using electron spin resonance, optical absorption and luminescence techniques, has revealed that most of these defects, in samples grown at low temperature ($\sim 1400^\circ\text{C}$), exhibit preferential alignment, i.e. a non-equal distribution over crystallographically equivalent orientations. Remarkably, this observation applies not only to defects assumed to involve only an Ni or a Co atom, but also to some Ni–N complexes. Annealing at $T > 1600^\circ\text{C}$ induces nitrogen mobility and the corresponding formation of numerous Ni–N- and Co–N-related centres. This annealing eventually destroys the preferential polarization of low-temperature centres.

1. Introduction

Single crystal diamonds grown by the high-pressure–high-temperature (HPHT) technique uniquely exhibit preferential polarization of some optical centres. In particular, previous optical absorption and photo- and cathodoluminescence (PL and CL) studies have revealed that:

- (1) The H3 centres, which comprise a pair of substitutional nitrogen atoms bordering a lattice vacancy ($[\text{N}_\text{S}-\text{V}-\text{N}_\text{S}]^0$, a centre of C_{2v} symmetry), are exclusively aligned to the [100] axis, but only in the {100} growth sectors (Collins 1992). It is important to note that this behaviour is not observed in natural diamond.
- (2) The 1.40 eV (Collins 1989) and 1.22 eV (Lawson *et al* 1993) optical centres, previously attributed to different charge states of an interstitial Ni-related defect (Lawson *et al* 1993,

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Nazare *et al* 1997), are exclusively aligned to the [111] axis in the {111} growth sectors, but not to the other equivalent $\langle 111 \rangle$ directions.

This unusual phenomenon of preferential defect alignment appears to be important for understanding the production and properties of defects in HPHT diamond, but, apart from the study of the 1.40 eV centre, has only been briefly explored in previous publications. In particular, it is important to know

- (1) whether other centres in HPHT diamond exhibit preferential alignment;
- (2) the symmetry and, ultimately, the microscopic structure of such defects; and
- (3) how stable the alignment is.

In an attempt to answer those questions, we have analysed, in this work, the orientations of a wide range of defects in HPHT diamond.

The following information is essential for the forthcoming presentation:

- (1) Ni and Co impurities are concentrated predominantly in the (111) growth sectors of HPHT diamond (Collins 1992, 1989, Lawson *et al* 1996).
- (2) Nitrogen predominantly incorporates in HPHT diamond grown at low temperature ($\sim 1400^\circ\text{C}$) as the N_5^0 donor centre of C_{3v} symmetry. This defect produces characteristic ESR (P1 centre) and optical absorption signals (Davies 1981), and acts as an electron donor, so charging most of the defects negatively. If vacancies are produced during the growth, they migrate towards the N_5^0 centres, thus creating $\text{N}_5\text{-V}$ complexes of C_{3v} symmetry (Davies 1981).
- (3) As a result of post-growth annealing at $T > 1600^\circ\text{C}$, nitrogen migrates, creating different Ni-N, Co-N, N_2 , and other nitrogen-related complexes (Lawson and Kanda 1993, Lawson *et al* 1996, Collins 1992).

2. Experimental details

Several dozens of HPHT diamonds, grown at relatively low temperatures ($\sim 1400^\circ\text{C}$) using either an Ni or Co metallic catalyst, have been studied. Those samples typically contained 100–300 ppm of N_5^0 centres. In many samples the nitrogen concentration was reduced down to 0.01–20 ppm by introducing a getter (Ti or Zr) into the growth chamber. Preferential alignment of Ni-related defects was assessed by ESR and polarization-resolved optical absorption, PL and CL. Because of their low absorption coefficients, the preferential alignment of Co-related centres could be characterized by luminescence only.

ESR spectra were recorded with a commercial Bruker Q-band (~ 33 GHz) spectrometer. In order to study the defect alignment in a single growth sector, it is preferred to cut that growth sector from a whole crystal. However, many of the ESR signals studied, including AB1, AB5, AB7 and KUL18, were rather weak. Therefore, they were studied in whole crystals, containing all eight (111) sectors, but with clearly different, though unknown, volumes. In contrast, the NOL1, W8 and P1 lines were sufficiently strong to be studied in samples cut predominantly from a single growth sector. The preferential alignment of the ESR centres was assessed by the following procedure:

- (1) The complete angular map of the centre was recorded for sample rotation in the $\{01\bar{1}\}$ plane.
- (2) The resonance field positions and relative line intensities were simulated with the 'epr.for' computer program (J Weil) and compared with the experiment.

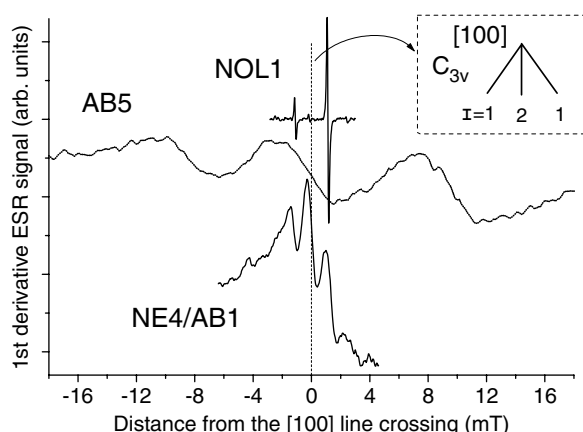


Figure 1. ESR spectra measured at 130 K in Q-band (~ 33 GHz) from as-grown Ni-rich HPHT diamond samples with the magnetic field direction tilted by a few degrees from the [100] axis in a $\{01\bar{1}\}$ plane. The insert shows a splitting pattern, i.e. field position versus angle from the [100] axis, predicted for a trigonal defect (C_{3v} symmetry) evenly distributed among the equivalent $\langle 111 \rangle$ directions. The observed relative intensities I clearly deviate from the predicted ones, thus revealing preferential defect alignment.

Optical measurements were performed on the (110) plates laser cut from the middle of whole crystals. After cutting, these sections were polished to an optical finish. A single (111) sector was further selected using a metallic mask. PL, CL and PL excitation (PLE) measurements were performed with custom-built spectrometers equipped with sheet polarizers and polarization scramblers. Special care was taken to avoid the distortions of polarization by the optics used. Optical absorption spectra were recorded with a commercial Perkin-Elmer Lambda 800 double-beam grating spectrometer. The light beam in this spectrometer is linearly polarized with an intensity ratio $I_{\parallel}/I_{\perp} \sim 10$. This property allowed us to study the polarized absorption simply by rotating the sample and consequently avoid using a polarizer, thus improving the signal-to-noise ratio and enlarging the accessible spectral range.

3. Experimental results and analysis

3.1. ESR spectra (Ni-doped samples)

The ESR spectra from our as-grown Ni-rich samples were dominated by the P1, W8, NIRIM1, NOL1, AB1/NE4, AB5 and AB7 centres (Pereira 2002, Neves *et al* 2000, Nadolinny *et al* 1997, 2002, Isoya *et al* 1990a, 1990b), and an apparently undocumented centre, which we label as KUL18. No preferential alignment was detected for the W8, NIRIM2 and P1 centres. This observation is not surprising: the W8 and NIRIM2 centres exhibit T_d symmetry (Isoya *et al* 1990a, 1990b), and the trigonal P1 centre, even if incorporated with preferential orientation, should have reoriented at the high temperatures of the growth (Davies 1981). In contrast, the NOL1, AB1/NE4, AB5, AB7 and KUL18 centres did show preferential alignment, as demonstrated in figures 1–3.

Figure 1 presents ESR spectra from the trigonal NOL1, AB5 and AB1/NE4 centres recorded for the magnetic field direction close to [100] in the $\{01\bar{1}\}$ plane. The observed intensity ratio clearly deviates from the 1:2:1 expected for trigonal centres evenly distributed among crystallographically equivalent $\langle 111 \rangle$ axes (see the inset in figure 1). The deviation is strongest for the NOL1 centre because the AB1/NE4 and AB5 centres (as well as the AB7 and

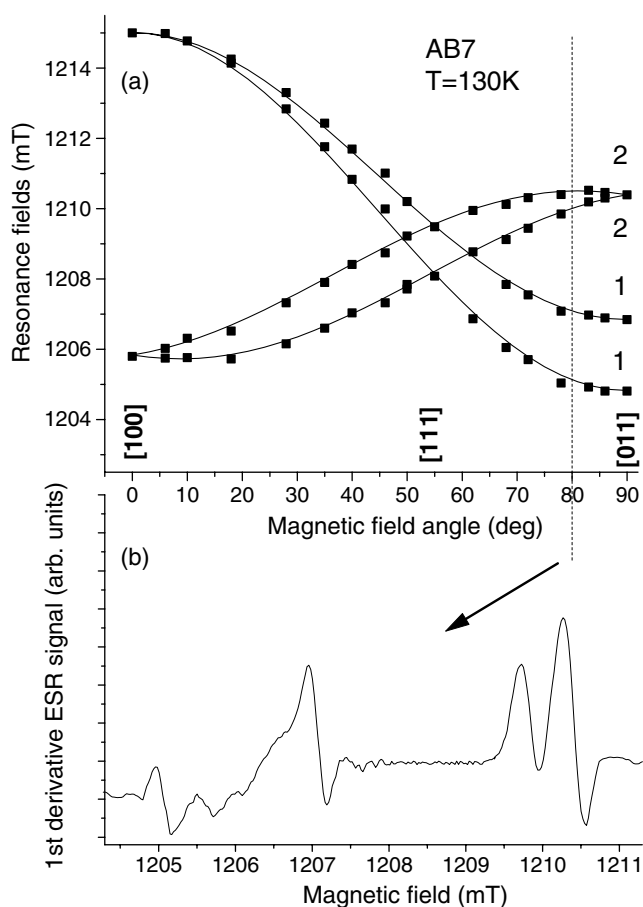


Figure 2. (a) The angular map of the AB7 centre measured for rotation in the $\{01\bar{1}\}$ plane at 130 K in Q-band (~ 33 GHz). Panel (b) presents a first-derivative ESR spectrum recorded with the magnetic field tilted 80° from the $[100]$ axis and shows a deviation of the relative line intensities from those predicted (numbers in panel (a)) for a defect evenly distributed among the equivalent orientations.

KUL18 centres in figures 2 and 3) were studied in complete crystals, but the NOL1 centre was investigated in a sample containing only two (111) sectors with very different volumes.

It is worth noting that a careful examination of previously reported spectra reveals a preferential alignment of the AB5 (Neves *et al* 2000) and NIRIM2 (Isoya *et al* 1990b) centres.

The complete angular maps of the NOL1, AB1/NE4 and AB5 centres, but not of the AB7 and KUL18 centres, have been reported previously (Nadolinny *et al* 2002, Neves *et al* 2000, Pereira 2002). Therefore, in panels (a) of figures 2 and 3 we plotted the angular maps of the AB7 and KUL18 centres, while panels (b) present characteristic ESR spectra for the magnetic field angle indicated by the dashed lines. The solid lines in panels (a) were calculated using the following spin-Hamiltonian parameters: $S = 1/2$, $g_1 = 1.9915(1)$ ($[100]$ axis), $g_2 = 2.0084(1)$ ($[011]$), $g_3 = 2.0050(1)$ ($[0\bar{1}1]$) for the AB7 centre and $S = 1/2$, $g_1 = 2.096(1)$ (11° tilted from the $[111]$ axis in the $\{01\bar{1}\}$ plane), $g_2 = 2.048(1)$ ($[01\bar{1}]$), $g_3 = 2.005(1)$ for the KUL18 centre. The numbers in panels (a) indicate the relative intensities calculated for the corresponding branches. They clearly do not match the relative line intensities in spectra (b), thus revealing that the AB7 and KUL18 centres are preferentially aligned.

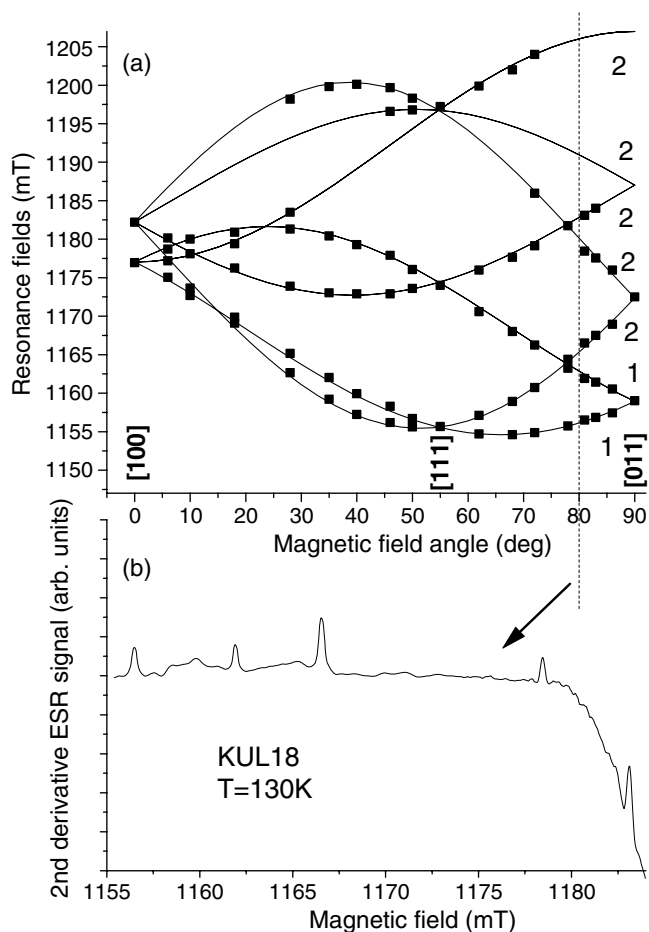


Figure 3. (a) The angular map of the KUL18 centre measured for rotation in the $\{01\bar{1}\}$ plane at 130 K in Q-band (~ 33 GHz). The lack of data in the ranges 1183–1197 mT, and > 1204 mT is due to masking by the strong W8 and P1 signals, respectively. Panel (b) presents a second-derivative ESR spectrum recorded with the magnetic field tilted 80° from the [100] axis and showing a deviation of the relative line intensities from those predicted (numbers in panel (a)) for a defect evenly distributed among the equivalent orientations.

It is worth noting that the spin-Hamiltonian parameters of the KUL18 centre are similar to those of the previously reported (Pereira 2002) AB6 centre. However, the corresponding angular maps differ somewhat, suggesting that those are two different centres. However, this conclusion is not final, as the angular map associated with the AB6 centre was measured under significant misalignment, thus making uncertain the validity of the reported fitting parameters. Regarding the AB7 centre, it is important that this centre was observed previously (Neves *et al* 2000) only in HPHT diamonds subjected to annealing at $T > 1700^\circ\text{C}$, which inevitably induced nitrogen aggregation. By contrast, we observe this centre, as well as KUL18, in HPHT crystals grown at low temperatures for which no evidence of nitrogen mobility could be detected by ESR and optical techniques. However, our diamonds contain only medium concentrations of N_S^0 centres (~ 20 ppm), which could be the key to the detection of the AB7 (and KUL18) centre. Indeed, accepting this suggestion, we can understand why it was necessary to anneal

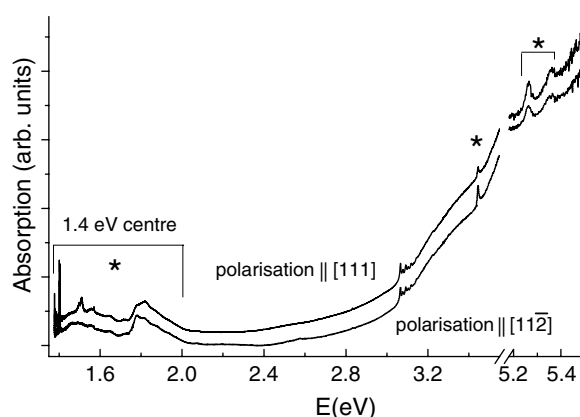


Figure 4. Optical absorption spectra (77 K) from an as-grown low-nitrogen, Ni-rich HPHT diamond measured with the incident light polarized along the [111] growth direction (top spectrum) and perpendicular to it (bottom spectrum). Asterisks mark the polarization-dependent lines. No sharp-line features were observed in the omitted 3.6–5.2 eV range.

nitrogen-rich diamonds in order to produce the AB7 centre in the previous study (Neves *et al* 2000)—the annealing could just serve as a means to reduce the N_S^0 concentration.

3.2. Optical measurements on as-grown Ni-rich samples

Luminescence spectra from our as-grown Ni-rich diamonds were dominated by the 1.40 and 2.56 eV systems (Collins 1992). The 1.40 eV centre exhibited strong polarization dependence, in agreement with the previous observations (Collins 1989). In contrast, the 2.56 eV luminescence appeared unpolarized either under unpolarized or linearly polarized excitation, thus suggesting T_d symmetry for this centre.

Optical absorption spectra from our as-grown Ni-rich diamonds were dominated by the previously reported 1.22, 1.40, 1.883, 2.51, and 3.1 eV centres, as well as by undocumented lines at 3.444 and 5.263 eV (low-nitrogen samples). Among those centres, the 1.22 (not shown), 1.40, 3.444 and 5.263 eV systems showed preferential polarization, as demonstrated in figures 4 and 5. The downward brackets in figures 4–6 indicate features belonging to one centre and the asterisks refer to the polarized centres. Note that previous uniaxial stress measurements assigned trigonal, C_{2v} and T_d symmetries to the 1.40 (Nazare *et al* 1997), 1.883 (Nazare *et al* 1996) and 2.51 eV (Nazare *et al* 2001) centres, respectively.

3.3. Optical measurements on annealed Ni-rich samples

In some as-grown nitrogen-rich samples an additional absorption line could be detected at 2.62 eV, and this line did show preferential polarization (see figure 5). After the sample used for figure 5 was HPHT annealed at 1800 °C the intensity of this line significantly increased; however, the preferential polarization was destroyed. The latter observation suggests that the 2.62 eV centres do reorient at $T \sim 1500$ –1800 °C; however, the observed intensity increase is yet unclear and can be explained by two different mechanisms:

- (1) The 2.62 eV centre does not involve nitrogen. Annealing merely reduces the concentration of N_S^0 centres via nitrogen aggregation, thus changing the Fermi level which enhances the detection sensitivity.

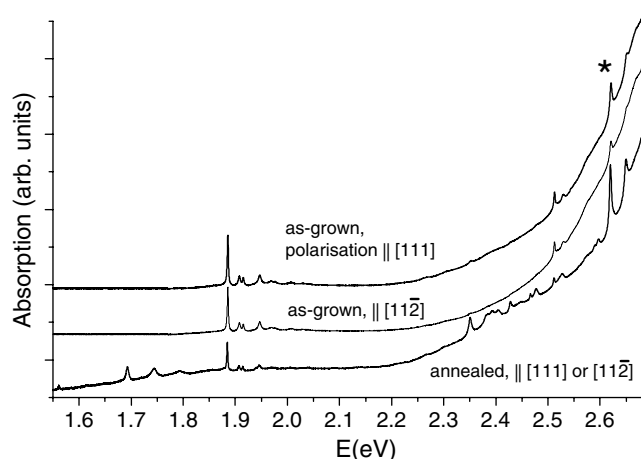


Figure 5. Optical absorption spectra (77 K) measured with the incident light polarized along the [111] growth direction and perpendicular to it from a high-nitrogen, Ni-rich HPHT diamond before and after annealing at 1800 °C. An asterisk marks the polarization-dependent line at 2.62 eV.

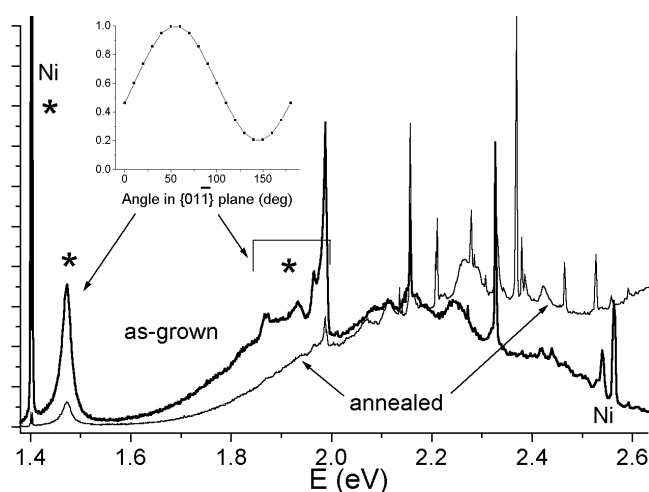


Figure 6. Cathodoluminescence spectra (77 K) from Co-doped HPHT diamond before and after annealing at 1600 °C. The sample exhibits CL from two Ni-related centres originating from accidental Ni contamination. Asterisks mark the polarization-dependent lines. The dependence of the 1.474 or 1.987 eV peak intensity on the polarizer angle, when rotated in the {011} plane, is shown by the inset.

- (2) The 2.62 eV centre is an Ni–N-related complex. During the annealing, single Ni-related centres trap moving nitrogen thereby forming the 2.62 eV centre.

Our results suggest that the second scenario is more plausible. Indeed, if (1) were true then the 2.62 eV centre should be detected in nitrogen-gettered as-grown samples, contrary to our observations. Meanwhile, ESR measurements on the as-grown sample used for figure 5 detected traces of another Ni–N-related centre NE1 (Nadolinny *et al* 1997), thus revealing that some minor Ni–N aggregation did occur during growth. This observation supports the Ni–N-related model (2) for the 2.62 eV centre. Accepting the Ni–N-related nature for the 2.62 eV centre, we arrive at an interesting conclusion that not only defects believed to involve

Ni only (1.40, 1.22 eV centres, etc), but also Ni–N complexes, can be aligned during the HPHT growth.

Apart from enhancing the absorption due to the 2.62 eV centre, the HPHT annealing produced a large number of ESR, absorption and luminescence signals, partly observed in figure 5 and reported previously (Lawson and Kanda 1993). Those signals have been associated with various Ni–N-related complexes (Lawson and Kanda 1993, Nadolinny *et al* 1997). As expected, none of those lines were polarized, because although during the synthesis the growth direction could be preferential, there is no obvious reason for that during annealing.

3.4. Appearance of Ni-related signals with increasing N_S concentration

Finalizing the characterization of Ni-related centres, we summarize the appearance, with gradually increasing concentration of N_S^0 donors, of the dominant Ni-related optical and ESR centres in our as-grown HPHT diamonds in the following table 1:

Table 1.

N_S^0 (ppm)	NOL1	1.22 (eV)	1.40 (eV)	2.56 (eV)	3.1 (eV)	NIRIM1	3.444 (eV)	5.263 (eV)	AB7	KUL18	1.883 (eV)	2.51 (eV)	W8	AB1	AB5
<0.1	+	+	+	+	+	+	–	–	–	–	–	–	–	–	–
~1	–	–	+	+	+	+	+	+	–	–	–	–	–	–	–
~20	–	–	–	–	–	–	–	–	+	+	+	+	+	–	–
>100	–	–	–	–	–	–	–	–	–	–	+	+	+	+	+

3.5. Luminescence measurements on Co-rich samples

Luminescence spectra from as-grown Co-rich samples were dominated by the Co-related 1.987 and 1.474 eV centres (see figure 6). The 1.40 and 2.56 eV Ni-related signals were present as well, most probably due to trace Ni impurities in the Co catalyst. This result supports a common opinion that Co incorporates in HPHT diamond much less efficiently than Ni (Lawson *et al* 1996). Two other lines at 2.156 and 2.33 eV, observed in the CL spectra of figure 6, are nitrogen-related and do not involve Co or Ni (Collins 1992). Only the 1.987 eV centre, but not the 1.474 eV centre, has been reported previously (Lawson *et al* 1996), although we observe both centres in all our Co- and N-doped samples. This can be simply attributed to the extended spectral range (1.37–6.2 eV) of the detector used in our CL system as compared to the narrower range (~1.5–6.2 eV) of the detector used by Lawson *et al*. Remarkably, the 1.987 and 1.474 eV systems exhibited very similar polarization behaviours, as presented in the inset of figure 6: when the analysing polarizer is rotated in the $\{01\bar{1}\}$ sample plane, the CL from those centres exhibits a pronounced maximum along the $[111]$ crystal axis. By contrast, the nitrogen-related 2.156 and 2.33 eV lines were unpolarized, despite the trigonal symmetry of the 2.156 eV system (Davies 1981).

Figure 6 also reveals that HPHT annealing at $T \sim 1600^\circ\text{C}$ reduced the intensity of the 1.40, 1.474 and 1.987 eV systems and produced lines at 2.135, 2.207, 2.227 and 2.367 eV previously associated with the Co–N complexes (Lawson *et al* 1996). Also, it was found that

- (1) the annealing destroyed the polarizations of the 1.474 and 1.987 eV lines, but not of the 1.40 eV centre;
- (2) none of the Co–N-related centres produced exhibited preferential alignment. The depolarization of the 1.40 eV centre occurred only after annealing at higher temperatures ($\sim 1800^\circ\text{C}$), thus revealing the enhanced reorientation stability of this centre.

3.6. Luminescence excitation measurements

The similar polarization behaviour and correlated appearance in different samples (section 3.4) has led us to the suggestion that the 2.56 eV luminescence and 3.1 eV absorption systems could originate at one Ni-related defect. By the same reasoning, 1.474 and 1.987 eV lines could originate at one Co-related defect. In order to test this hypothesis, PL excitation spectra have been measured for the 2.56, 1.474 and 1.987 eV lines. The spectra will be presented and analysed elsewhere, and they can be summarized as follows: the 3.1 eV system appeared in the PLE spectrum of the 2.56 eV system and the PLE spectra from the 1.474 and 1.987 eV systems were virtually identical. These observations support the above hypotheses. The appearance of the 3.1 eV system in the 2.56 eV PLE spectrum has been noticed previously by Spear (1990).

4. Summary and conclusions

A comprehensive study of Co-, Ni-, and nitrogen-related centres in HPHT diamond, using ESR and optical techniques, has revealed that the preferential alignment, previously reported for the 1.40 eV (Collins 1989), 1.22 eV (Lawson *et al* 1993) and H3 (Collins 1992) centres, is not a curiosity, but is a common phenomenon in HPHT diamond, which can be summarized as follows:

- (1) Many Ni- and Co-related defects are preferentially aligned to the [111] axis in the {111} growth sectors of low-temperature grown HPHT diamonds. Remarkably, this observation applies not only to defects believed to involve just Ni or Co atoms, but also to at least one Ni–N complex, namely the 2.62 eV absorption centre. The exceptions are the W8 and NIRIM1 ESR centres, lines at 2.56 eV (luminescence) and 2.51, 3.1 eV (absorption), all of T_d symmetry, and the 1.883 eV absorption centre of C_{2v} symmetry.
- (2) In contrast, the nitrogen-related P1 ESR centre, and luminescence lines at 2.156 and 2.33 eV, appear unpolarized, despite the trigonal symmetry of the former two centres. This result can be understood as all those centres could easily reorient at the growth temperatures (Davies 1981), even if introduced with preferential orientation.
- (3) Annealing at $T > 1600^\circ\text{C}$ induces nitrogen mobility and the corresponding formation of numerous Ni–N- and Co–N-related centres, and eventually destroys preferential polarization of low-temperature centres.

In addition, the reported PL and PLE results suggest that the 2.56 eV luminescence and 3.1 eV absorption system originate at the same charge state of the same Ni-related centre of T_d symmetry and that the 1.474 and 1.987 eV luminescence peaks belong to the same Co-related defect.

Acknowledgments

The authors are indebted to H Kanda (NIMS, Japan), A Taylor (DTC research centre), and I Kiflawi (Reading University) for the provision and preparation of samples. KI is grateful to the Belgian FWO for financial support.

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