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Photochromism of vacancy-related centres in diamond

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Abstract. Optical experiments, involving photoluminescence (PL), the PL excitation and quenching spectra, as well as transmission and its quenching, were used to analyse the photochromic behaviour of some vacancy-related complexes in diamond. The 2.156 eV, 1.945 eV and 1.68 eV optical centres in CVD diamond are attributed to the neutral nitrogen–vacancy, negative nitrogen–vacancy and neutral silicon–vacancy ([Si–V]⁰) centres, respectively. Oscillatory behaviour in the excitation spectrum of the 1.68 eV luminescence is observed and from the threshold of the oscillations a position of $E_C - 2.05$ eV is suggested for the ground state of the [Si–V]⁰ centre.

1. Introduction

Optical methods are widely used for defect identification and characterization in diamond (Walker 1979). Resonant transitions caused by internal excitation of a defect centre (without its ionization) lead to the appearance of several narrow absorption and luminescence lines: the zero-phonon line (ZPL) and associated vibronic features. Finding a correlation of ZPLs with specific defect centres has proven to be a challenging problem in the experimental study of diamond. Such identification is complicated by the fact that different optical centres in diamond do have similar ZPL energies. Typical examples are the so-called S1, H3 and 3H defects, all having the same position of the ZPL at 2.463 eV (Walker 1979), and centres with ZPLs around 1.68 eV (Kiflawi *et al* 1997). In addition, the ZPL position may be shifted by stress, which is often present in artificial diamonds, and can lead to a mistaken identification. Therefore, a comprehensive study of the ZPL and its vibronic structure by a combination of absorption and emission methods is needed to distinguish between the different centres.

A further complication in identifying luminescent centres arises from the fact that different optical bands may belong to the different charged states of the same defect (Collins and Rafique 1979, Mita *et al* 1990, 1993, Mita 1996). In typical semiconductors (like Ge, Si etc) most defect centres form shallow, or highly delocalized states in the forbidden gap. However, in diamond, due to the extreme rigidity of the lattice, most defects form deep centres, which may have different optical transitions for differently charged states. Such centres can be recognized by their photochromic behaviour: concentrations of differently charged states of the centre may be changed by the shift in the Fermi level position caused by doping, additional illumination etc. Several photochromic centres are known in diamond: H3 and H2 centres (Mita *et al* 1990, 1993) which are attributed to the neutral and negative states of a vacancy trapped by two nitrogen atoms ([N–V–N]⁰ and [N–V–N][–]), the GR1 and ND1 defects (Walker 1979), being

ascribed to $[V]^0$ and $[V]^-$, and the 2.367 eV and 1.979 eV centres (Collins and Rafique 1979). Another possible photochromic centre is the nitrogen–vacancy ($[N-V]$) complex, with ZPL at 1.945 eV for the negative state (Walker 1979). Changes in the absorption of the 2.156 eV and 1.945 eV centres after neutron irradiation were reported by Mita (1996). They were attributed to the shift in the Fermi level position but not to the variation in the concentrations of these centres. A hypothesis that the 2.156 eV centre originates from the neutral charge state of the $[N-V]$ complex was suggested.

In this study we report on the photochromic behaviour of these 2.156 eV and 1.945 eV centres in CVD diamond by means of measurements of photoluminescence (PL) and optical transmittance with additional illumination. We also present analogous results for the 1.68 eV centre and will argue that they can be interpreted in terms of a photochromic $[Si-V]$ complex. Oscillatory behaviour observed in the PL excitation (PLE) spectrum of the 1.68 eV centre will also be discussed.

2. Experimental details

Diamond films were grown in an ASTeX PDS-17 microwave plasma reactor at the Institute for Materials Research, Diepenbeek, Belgium (Nesladek *et al* 1996) and at Nanyang Technological University, Singapore. All samples were grown on Si substrates, which were removed by chemical etching in $HNO_3:HF$ mixture after the diamond film deposition. Material studied was nominally undoped; nevertheless, PL spectra show the presence of nitrogen and silicon in the films. The contamination by nitrogen and Si is typical for CVD diamond. It originates from insufficient vacuum in the CVD reactor and from the plasma etching of silicon substrate and quartz walls of the reactor, respectively (Nesladek *et al* 1996). Micro-Raman spectroscopy was utilized to monitor the sp^2 carbon content in the films studied. Measurements were performed in reflection mode at 300 K, using a Dilor triple XY spectrometer with a nitrogen-cooled CCD detector and the 2.41 eV (514.5 nm) line of an Ar^+ laser focused to a 2 μm diameter spot. The ratio of integrated non-diamond carbon peaks to integrated diamond peak was used to compare the sp^2 carbon content in different samples. All results, except for those presented in figure 2, were obtained on good-quality films with a narrow (about 2 cm^{-1}) diamond Raman peak and undetectable non-diamond carbon phases. In the samples used for figure 2 the enhancement in amorphous carbon content was achieved by increasing the CH_4 flow rate during the film deposition while keeping other growth parameters fixed.

PL was induced by the 2.41 eV and 2.54 eV lines from an Ar^+ laser. PLE spectra were measured at 77 K using a double monochromator with a 250 W halogen lamp in the range 1.6–3.3 eV or a 150 W Xe lamp in the range 3.3–4.5 eV. To check the system performance we performed PLE measurements on the 2.156 eV and 1.945 eV optical centres. The resulting spectra were coincident with those reported by Walker (1979) with all features resolved. PLE measurements at 4.9 eV (254 nm) and 5.6 eV (220 nm) were performed using a 200 W Hg lamp and a 150 W Xe lamp, respectively, with a single monochromator and interference filter. In absorption experiments, light from a 50 W halogen lamp was dispersed by a 0.25 m Oriel monochromator before the sample in order to avoid additional illumination from the main source. Photochromic changes in PL and transmittance were induced by additional light from a 150 W Xe lamp dispersed by another 0.25 m monochromator. The main (exciting) light was modulated at 70 Hz and the detection system was resonantly tuned to this frequency. While additional light was not modulated and should not be detected, care was taken to avoid the influence of this light on the detection system. No significant heating of the sample was induced by additional illumination. Due to setup limitations only room-temperature measurements could be performed when added light was used. Two kinds of spectrum have been measured:

varying the wavelength of additional illumination at a fixed wavelength of PL or transmittance registration, denoted hereafter as PL or transmittance quenching (PLQ or TQ) spectra, and varying the wavelength of PL or transmittance registration at fixed wavelength of additional illumination.

3. Experimental results

Figure 1(a) shows PL emission from the 1.945 eV and 2.156 eV centres measured at 77 and 300 K. Figure 1(b) presents changes in intensity of room-temperature PL from these centres under additional illumination with the photon energy of 2.8 eV and 3.7 eV. It shows that 2.8 eV light leads to the simultaneous and equal increase in the 2.156 band PL and decrease in the 1.945 eV band intensity, while 3.7 eV light induces the opposite changes. These changes were reproducible for multiple illumination cycles, thus only one is shown in figure 1(b). PL spectra, measured at room temperature, with and without 2.8 eV illumination, along with the magnified difference spectrum are shown in figure 1(c). Analogous results were obtained for 3.7 eV illumination. It is seen that the change in the intensity of the 2.156 eV system is matched by an almost equal change in the 1.945 eV signal strength, which can be considered as evidence of a charge transfer between two different charge states of the same centre. Given that the 1.945 eV line is attributed to the negative state of the N–V centre and taking into account that the 2.156 eV and 1.945 eV centres have the same symmetry (Walker 1979, Mita 1996), the 2.156 eV system can be then ascribed to the neutral state of the [N–V] centre. The alternative would be an [N–V]²⁻ structure, which is rather improbable on microscopic grounds (Walker 1979).

Variations in the intensity of PL from the 2.156 eV, 1.945 eV and 1.68 eV centres in samples with different amorphous carbon (a-C) content are shown in figure 2. It is seen that the increase in the a-C related Raman band at 1550 cm⁻¹ from figure 2(a) to figure 2(c) results in the decrease of the amplitude of the 1.945 eV and 1.68 eV bands relative to the 2.156 eV system and the diamond Raman peak. While only results for three selected samples are shown, this tendency was observed on a larger number (more than 30) of samples.

Spectral dependencies of the photoinduced changes in the 2.156 and 1.945 eV PL intensities are shown in figure 3 as a function of the energy of the inducing photons. The inset shows the spectral dependence of the quenching source, measured by a wavelength-independent Golay detector. PL was excited at 2.41 eV. As normalization of PLQ and TQ spectra to the quenching light intensity led to a large uncertainty in the results in the UV region due to the small intensity of the quenching light, all spectra are normalized with respect to the PL or transmittance signal without additional illumination. The mirror-like symmetry between the graphs for the 1.945 eV (curve 1) and 2.156 eV (curve 2) systems, which is seen in figure 3, supports the interpretation and conclusions that were suggested by the data of figure 1 about the charge transfer between the [N–V]⁰ and [N–V]⁻ states.

Also presented in figure 3 are photoinduced changes in transmittance and PL of the 1.68 eV line. The two graphs were indistinguishable within the experimental resolution and are both shown by curve 3. The increase in absorption should correspond to the increase in PL but *decrease* in transmittance; therefore, changes in transmittance are shown as transmittance quenching (TQ) in the figure. We have presented some of these results in our earlier paper (Iakubovskii *et al* 1999) but would like to call attention here to the remarkable similarity between the PLQ and TQ spectra for the 2.156 eV and 1.68 eV lines. Moreover, the mentioned spectra coincide with the TQ curves for the broad a-C related absorption band with a threshold at about 1 eV (Nesladek *et al* 1996), measured at different energies (1.3, 1.4, 1.5 and 1.6 eV, all resulting in curve 4 of figure 2).

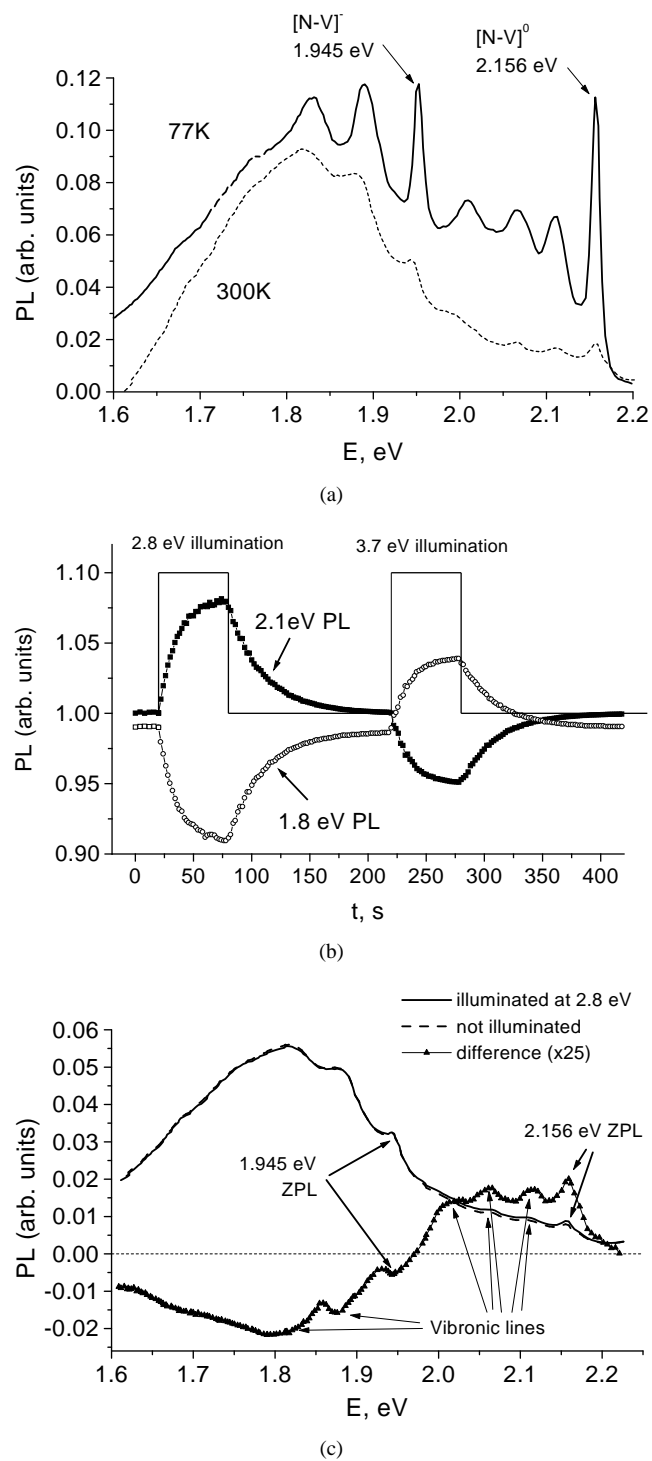


Figure 1. (a) PL emission from the 1.945 eV and 2.156 eV centres measured at 77 and 300 K. (b) Normalized changes in PL measured at 2.1 eV and 1.8 eV at 300 K under additional illumination with the photon energy of 2.8 eV and 3.7 eV. (c) Room-temperature PL spectra with and without 2.8 eV illumination, and the difference spectrum.

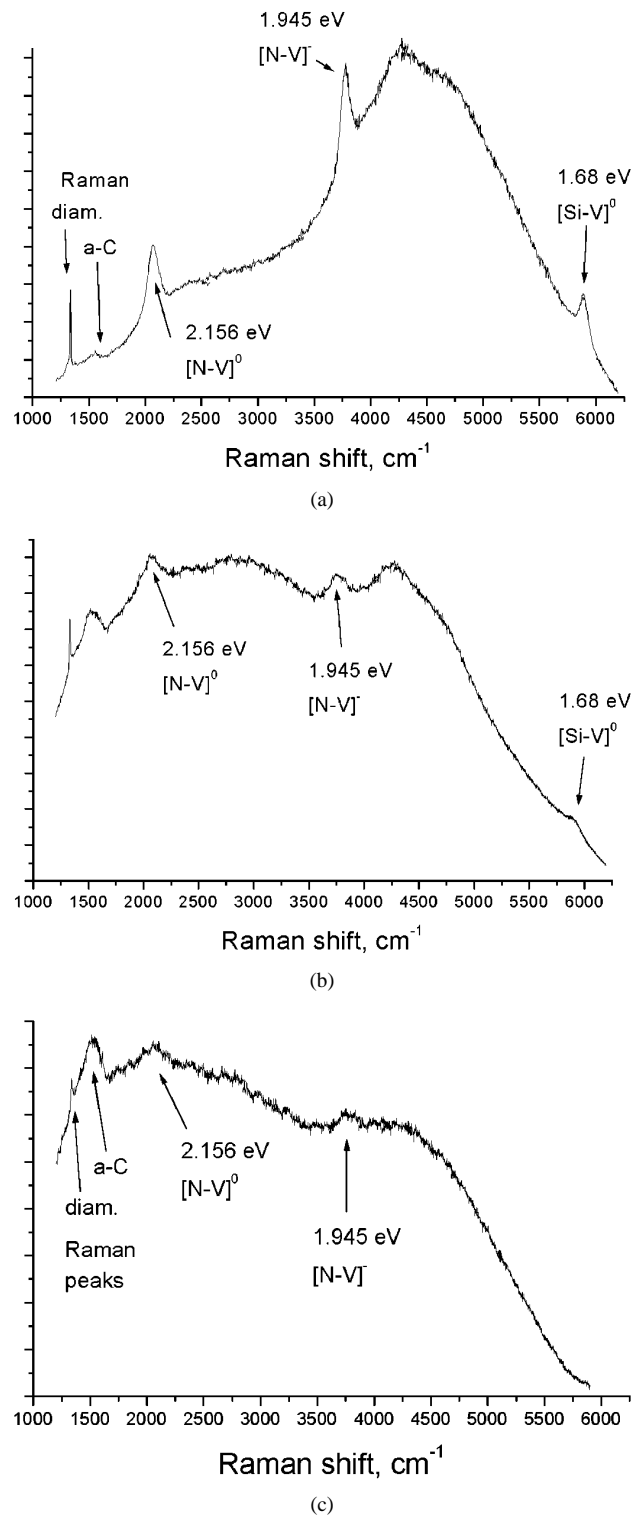


Figure 2. Room-temperature Raman and PL spectra under 2.41 eV excitation. CH₄ flow rate and a-C concentration in the film increases from (a) to (c).

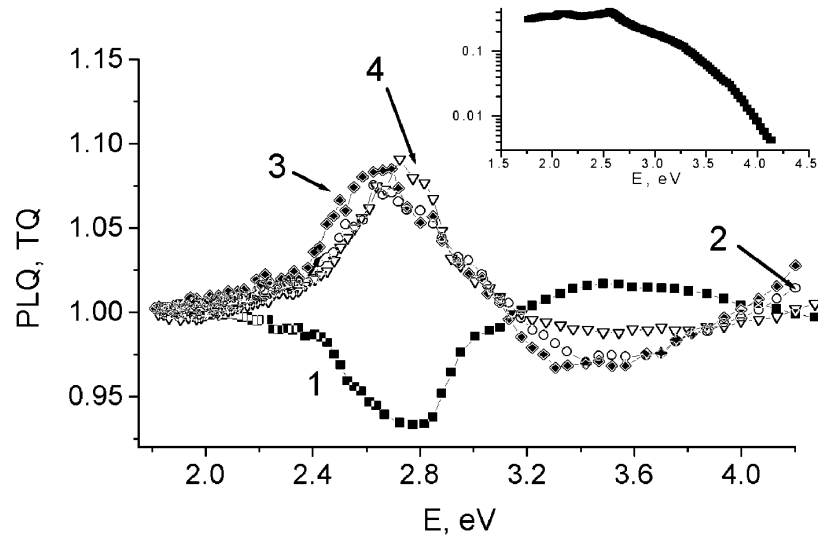


Figure 3. Quenching spectra of the room-temperature PL, excited at 2.4 eV, and transmittance (PLQ and TQ) for a CVD film: 1 (—■—) PLQ measured at 1.945 eV, 2 (—○—) PLQ at 2.156 eV, 3 (—◆—) PLQ and TQ at 1.68 eV, 4 (—▽—) TQ at either 1.3, 1.4, 1.5 or 1.6 eV. The inset shows the spectral dependence of the quenching source measured by a spectrally independent Golay detector.

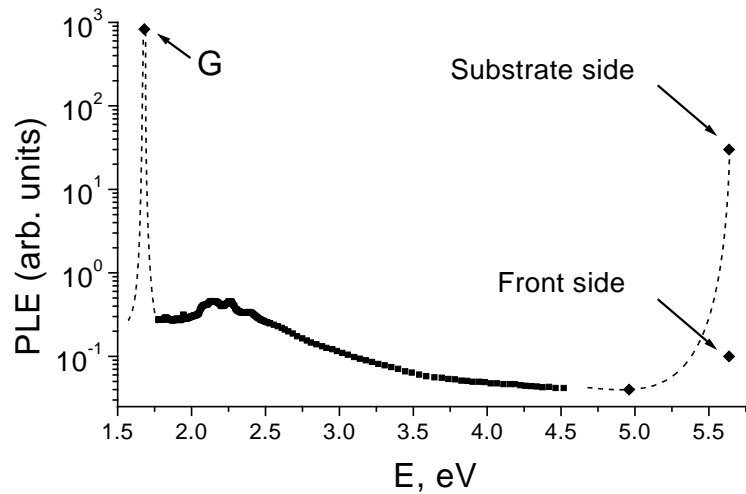


Figure 4. PLE spectrum of the 1.68 eV line measured at 77 K. Point G is taken from data of Gorokhovskiy *et al* (1995). Dashed lines are just guides for the eyes.

In figure 3 the change in the transmittance of the 1.68 eV line is about 10 per cent. However, it was found that an increase in the intensity of additional UV light might enhance the 1.68 eV absorption up to tenfold. This change is completely reversible and shows a very slow relaxation (up to several hours) after switching off the additional light. As discussed later, it can be interpreted in terms of an increased occupation of the ground state of the 1.68 eV centre upon illumination.

Further information that helps in the characterization of the 1.68 eV centre is contained in figures 4 and 5. Figure 4 shows the 77 K PLE spectrum of the 1.68 eV line with some structure

around 2.0–2.5 eV and a sharply increased sensitivity for 5.6 eV band-to-band excitation. That the relative intensity of the 1.68 eV luminescence excited at 5.6 eV is much higher at the substrate side than at the front side of a diamond film is believed to be due to the strong decrease in the concentration of Si atoms, responsible for the 1.68 eV PL, from the substrate to the front side in CVD films grown on Si (Dollinger *et al* 1995). The point G, which is also shown in figure 4, represents the observation by Gorokhovskiy *et al* (1995) that the vibronic band of the 1.68 eV line is 2500 times more intense under 1.68 eV than under 2.41 eV excitation. It illustrates that emission from the 1.68 eV centre can be even more efficiently produced via its internal excitation than via band-to-band excitation.

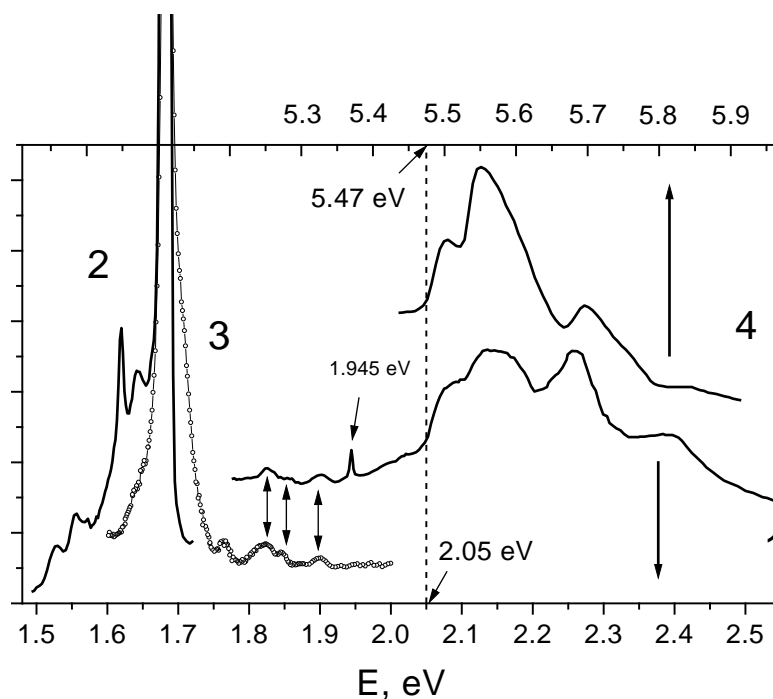


Figure 5. Details of the PLE spectrum from figure 4. Curve 1—PLE spectrum; curves 2 and 3—luminescence and absorption spectra of the 1.68 eV system; curve 4—PLE spectrum of the broad blue band in natural diamond in the range of intrinsic absorption (note the different x -axis) taken from data of Dean and Male (1964).

Details of the PLE spectrum from figure 4 in the range 1.8–2.6 eV are presented by curve 1 in figure 5. Also shown are luminescence (curve 2) and absorption (curve 3) spectra of the 1.68 eV system. Curve 4 presents a PLE spectrum of the broad blue band in natural diamond in the range of intrinsic absorption (note the different x -axis) taken from the data of Dean and Male (1964). The sharp peak at 1.945 eV in curve 1 is due to the 1.945 eV band underlying the 1.68 eV system. The PLE spectrum represented by curve 1 of figure 5 was reproduced on several samples; in each case the signal from the background band (different for different samples) was measured independently and subtracted, but the sharp peak at 1.945 eV is left as a marker of spectral resolution and energy calibration. In the range 1.8–1.9 eV the PLE spectrum shows several small peaks whose positions correlate with those of the vibronic features of the 1.68 eV centre seen in absorption (curve 3) and probably corresponding to PLE via electron–phonon vibronic transitions. These transitions are also seen in PL emission (curve 2).

Table 1. Parameters of photochromic vacancy-related centres in diamond.

| Defect | ZPL energy (eV) | Structure | Possible to observe in | | | Reference |
|--------|--------------------|----------------------|------------------------|----|-----------------|--------------------------------------|
| | | | absorption | PL | CL ^a | |
| GR1 | 1.673 | V ⁰ | + | + | + | Walker 1979 |
| ND1 | 3.15 | V ⁻ | + | - | - | Walker 1979 |
| H3 | 2.463 | [N-V-N] ⁰ | + | + | + | Mita <i>et al</i> 1990, 1993 |
| H2 | 1.267 | [N-V-N] ⁻ | + | + | - | Mita <i>et al</i> 1990, 1993 |
| | 2.156 | [N-V] ⁰ | + | + | + | Mita 1996, this work |
| | 1.945 | [N-V] ⁻ | + | + | - | Walker 1979, this work |
| | 1.68 | [Si-V] ⁰ | + | + | + | Collins <i>et al</i> 1994, this work |

^a Or in PL excited by UV light with energy exceeding the band gap (5.47 eV).

4. Discussion

In table 1 we summarize some of the characteristics of known vacancy-related photochromic centres in diamond, together with our proposal for the corresponding parameters of the centres discussed in this work. Concerning the 1.945 eV line, it may be pointed out that it should not be confused with the 1.968 eV line, which is frequently observed in nitrogen-doped CVD films. Although those lines are often seen together, and line shift and broadening may lead to their overlapping, they do belong to different centres. The 1.945 eV line was never observed in cathodoluminescence (CL), while the 1.968 eV is typically seen in CL emission (Ruan *et al* 1991). One noticeable fact which follows from table 1 is that, while the neutral states of the vacancy-related centres are seen in PL and CL, none of the negatively charged states are observed under excitation energy exceeding the diamond band gap (5.47 eV) in CL or UV PL experiments. Indeed, such an excitation should ionize the negative centres, leading to their transition to neutral states. That the 1.945 eV and 2.156 eV centres, whose photochromic behaviour is already demonstrated by the results in figures 1 and 2, follow this pattern lends further support to their designation as [N-V]⁻, respectively [N-V]⁰. Support for these assignments is also provided by changes in the luminescence intensity of the 1.945 eV and 2.156 eV lines with boron doping (Freitas *et al* 1994). Changes in the Fermi level position will then influence the occupation of the differently charged states, with the negatively charged [N-V]⁻ losing intensity first, as indeed observed. An alternative scenario, which would ascribe the intensity loss to the incorporation of boron atoms into the vacancy sites, would cause a joint decrease of [N-V]⁻ and [N-V]⁰ PL, which was not observed in experiment. Further evidence in favour of the proposed interpretation can be seen in figure 2, revealing the decrease in the 1.945 eV band relative to the 2.156 eV system with the increase in the a-C content in a diamond film. Indeed, the a-C related defects could play the role of centres which shift the Fermi level position down to approximately the $E_V + 1$ eV level (Robertson 1996, Nesladek *et al* 1996). This, as in the case of boron doping, would again lead to the conversion of [N-V]⁻ to [N-V]⁰.

The striking similarity of transmission and PL quenching spectra for different centres shown in figure 3 implies that the photochromic changes in these centres occur not by their direct photoionization, but via capture of electrons and holes generated in the conduction and valence bands (CB and VB) via photoionization of some dominant defect centre. Since a-C is found to be the dominant absorption centre in CVD diamond, even if no a-C related bands are present in Raman spectra (Nesladek *et al* 1996), the changes in PL and transmittance shown in figure 3 can possibly be ascribed to different absorption transitions between the π , π^* , σ and σ^* states of a-C analysed by Nesladek *et al* (1996). A similar mechanism, possibly with another dominant absorption centre, could also be responsible for the changes in absorption

(Collins and Rafique 1979, Mita *et al* 1990, 1993, Mita 1996) and electron spin resonance (ESR) signals (Rohrer *et al* 1996, Mita *et al* 1998) with additional illumination observed in natural and CVD diamond.

Another photochromic defect mentioned in table 1 is the 1.68 eV centre. Experiments on Si ion implantation in natural diamond (Vavilov *et al* 1981) have shown that this centre, which can be distinguished from others (Kiflawi *et al* 1997) with ZPL around 1.68 eV by its characteristic phonon structure (Feng and Schwartz 1993), is Si related. The symmetry of the 1.68 eV centre suggests a more complex structure than a single Si atom, but at least two defects oriented along the $\langle 110 \rangle$ axis (Brown and Rand 1995). Collins *et al* (1994) showed that the 1.68 eV absorption grows when vacancies anneal out and suggested that this centre originates from an [Si–V] complex. There are some striking similarities between the 1.68 eV and the 1.673 eV (neutral vacancy, GR1) centres:

- (1) both centres are vacancy related and could be observed in absorption, PL and CL;
- (2) they have almost the same emission energies;
- (3) the ground and first excited states for both centres are split into two levels: values of splitting are 8 meV and 20 meV for the 1.673 eV (Clark and Walker 1973) and 0.2 and 1 meV for the 1.68 eV (Clark *et al* 1995) centres, respectively.

The data in figure 3 further reveal that the 1.68 eV line behaves under additional illumination similarly to the $[\text{N–V}]^0$ centre. All these arguments suggest that the charge state of the 1.68 eV state of the [Si–V] centre can be considered as neutral. The experimental fact that UV light can strongly change the population of the 1.68 eV state means that another charge state of the [Si–V] complex prevails in equilibrium. Accepting that all known vacancy-related complexes in diamond do not form negative- U centres (Walker 1979), we tentatively suggest this state to be positive. Unfortunately, no PL or absorption line, with an intensity comparable with the one of the 1.68 eV line, and which changes under additional illumination in accordance with the changes in the 1.68 eV line, was observed in the range 1.2–4 eV in our samples.

The stability of changes in the 1.68 eV transmittance induced by UV light shows that special care should be taken when drawing conclusions about the absence of some defect or when comparing deep centre concentrations in different samples on the basis of experiments which detect occupied defect centres, like optical absorption, PL, ESR etc. The Fermi level position and the history of light and heat treatment may be different from sample to sample, leading to a change in the occupation of defect centres. In PL and CL experiments the equilibrium distribution of the level occupations is disturbed by the excitation source, but the degree of this change may also depend on the dark Fermi level position and its pinning by other defects. To check the latter, we performed PLQ and TQ experiments at 1.68 eV on samples showing similar intensity of the 1.68 eV absorption but with different amorphous carbon content. In this series, the a-C-related defects would play the role of centres which pin the Fermi level position (Robertson 1996). A similar shape of PLQ and TQ spectra was observed for all samples; however, the intensity of peaks gradually decreased, at constant linewidth, with the increase in a-C content. The decrease in the 1.68 eV PL with the increase in the a-C content (see figure 2) may also be considered as evidence of changes induced rather by the Fermi level shift than by the variation in the Si content in a film. The latter is rather unlikely, because the incorporation of Si atoms into diamond film should be governed by the growth conditions, which were approximately the same for all samples used for figure 2.

Remarkable is the oscillatory structure in the 2.0 to 2.5 eV region in the PLE of the 1.68 eV centre shown by curve 1 in figure 4. Such oscillations were observed in excitation spectra of PL (Dean and Male 1964, Male 1961, Dehnam *et al* 1967), photoconductivity (Dehnam *et al* 1967, Rohrer *et al* 1998) and photoelectron yield (Bandis and Pate 1995a, b) in natural and

CVD diamond, for both band-to-band and band-to-defect-level transitions. They are explained by phonon-assisted modulation of the carrier lifetime when a carrier is excited to the VB or CB: if the excited state of a defect in the forbidden gap lies close to the edge of the VB or CB, there is enhanced transition probability of a photoexcited carrier from the band to this state by cascade emission of phonons, without thermalization of the carrier to the bottom of the band. This probability has maxima when the energy to dissipate is a multiple of the phonon energy and leads to the maxima in PLE and minima in photoconductivity excitation spectra (Dehnam *et al* 1967). The oscillations in the PLE spectrum of curve 1 in figure 4 occur at energies much lower than the band gap of diamond, and therefore should be attributed to transitions from the ground state of some defect centre to the CB. The existence of excited states close to the CB for this centre, which is necessary for the oscillatory behaviour, is seen in both absorption and PLE spectra (marked by double-ended arrows in figure 5). In analogy with the model of photochromic changes discussed above, it is reasonable to suggest that the electron in the CB is generated from some dominant defect centre and then captured by an excited state of the 1.68 eV centre. However, for such a generation mechanism one would expect to observe the same position and shape of PLE oscillations for different optical centres in the same sample. The latter is not observed: our PLE measurements reveal that different optical centres in the same CVD film show different positions of the PLE threshold and various shapes of oscillations. Such deviations in the shape could be attributed to the difference in the excited state structure for different optical centres and will be discussed elsewhere. We, therefore, suggest that the electron captured by the excited state of the 1.68 eV centre may have been generated from the ground state of the same centre. Some kind of localization must then exist: the generated electron should have a non-zero probability of being captured by the centre before it moves away in the conduction band.

The oscillatory structure allows us to make a proposal for the position of the 1.68 eV centre in the diamond band gap. By aligning, as done in figure 4, the PLE spectrum shown by curve 4 with its characteristic threshold at 5.47 eV, corresponding to the energy of the indirect band gap of diamond, with a corresponding threshold on curve 1, we then obtain a difference of 2.05 eV between the bottom of the CB and the ground state of the 1.68 eV centre.

5. Summary and conclusions

Based on the results of spectrally resolved measurements of photochromism in the 2.156 eV, 1.945 eV and 1.68 eV centres in CVD diamond, we have attributed these complexes to the $[N-V]^0$, $[N-V]^-$ and $[Si-V]^0$ states respectively. The absence of the cathodoluminescence emission from the negatively charged centres in diamond is explained by the ionization of these centres. It is further suggested that in equilibrium, $[Si-V]$ centres in the CVD films studied mainly occupy the positively charged states. Oscillatory behaviour which is observed in the excitation spectrum of luminescence from the 1.68 eV line was interpreted as due to resonant transitions of electrons from the conduction band to the excited state of the 1.68 eV centre by emission of a number of phonons. From the threshold of PLE oscillation, we suggest $E_C - 2.05$ eV as the position of the ground state of this centre.

Acknowledgments

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