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Effect of oxygen on the cathodoluminescence signal from excitons, impurities and structural defects in homoepitaxial (100) diamond films

M. Kadri[a], D. Araujo[a,b], M. Wade[a], A. Deneuville[a,*], E. Bustarret[a]

[a]LEPES-CNRS and University of Grenoble, 25 Avenue des Martyrs, B.P. 166, 38042, Grenoble Cédex 9, France
[b]Universidad de Cádiz, Dpto. Ciencia de los Materiales e IM y QI, Spain

Abstract

Cathodoluminescence at 5 K is used to study the residual radiative defects in homoepitaxial diamond films deposited on the centre of the plasma ball versus the O/CH_4 ratio from 0 to 0.375 in the feeding gas, and to understand their effect on the quality (intensity of the free exciton peaks) of the films. The addition of oxygen significantly reduces the slight boron contamination (1.6×10^{16} to 4×10^{14} cm^{-3}) of these good quality (BE^{NP} exciton peak) non-intentionally doped films. As the O/C ratio increases, (i) the intensities of the boron-bound excitons, Nc–Vc, H3, Nc–Ic peaks, of the 2.3 eV wide band and the nitrogen contamination decrease (ii) the intensity of the N3 peak and the relative intensity of the A band increase. These opposite variations of the defects concentration as O/C increases result in a maximum of the FE peaks for O/C around 0.25.

Keywords: CVD diamond; Oxygen; Cathodoluminescence; Excitons

1. Introduction

With the increasing interest for diamond in electronic devices, the quality of undoped or p-type diamond films becomes an important challenge. While deposition at 800 °C with very low methane content associated to low surface misorientation and roughness of the substrate very significantly improves the film quality, it results in very low deposition rates (20–50 nm/h) and difficulties to incorporate boron in the film [1]. A higher deposition temperature and the addition of oxygen in the plasma were shown to improve the quality of the diamond polycrystalline films [2,3]. Therefore, we look for an alternative way to improve the quality of the homoepitaxial films, with a higher deposition temperature of 900 °C and a higher methane content of 1% and the addition of oxygen to the feeding gas, while keeping the possibility of easy boron incorporation. Cathodoluminescence was used to check both the quality of the films [1,2] and the nature of their main residual radiative defects [1–3].

2. Experimental techniques

The films were deposited during 9 h on standard 3×3 mm Ib substrates at 900 °C in a NIRIM type deposition chamber evacuated in the 10^{-6} torr range by a turbo molecular pump before the admission of gas mixtures containing 1% of CH_4 and 0%, 0.25% and 0.375% of O_2 at a pressure of 50 torr and a total flow rate of 200 sscm. The Ib substrates are lying in the centre of the plasma ball on Si substrates holders covered with thick polycrystalline diamond films.

The cathodoluminescence spectra were collected at 5 K in a Quanta 200 Scanning Electron Microscope (SEM) coupled through a home-made mirror to the 50-μm-wide slit entrance of a HR 460 Jobin Yvon grating (600 g/mm) monochromator equipped with a liquid N_2-cooled CCD array. The spectra were excited with a 10-kV electron beam.

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* Corresponding author. Tel.: +33 4 76 88 10 09; fax: +33 4 76 88 79 88.
E-mail address: deneuvil@grenoble.cnrs.fr (A. Deneuville).

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The pixel-to-pixel spectral spacing was 0.09 nm (2.0 meV around 5.25 eV).

3. Results

Fig. 1 shows the full cathodoluminescence spectrum (with a local scale expansion around BE^{TO} and BE^{NP} in the A and B insets) of the sample deposited without oxygen in the 4.9–5.4 eV exciton energy range. It exhibits peaks around 5.353, 5.319, 5.265, 5.215, 5.104, 5.045 and 4.94 eV. From 5.353 down to 5.215 eV, the peaks are very narrow (4, 6, 6, 8 meV). As their energy decreases, they widen around 22 and 24 meV for the 5.104 and 5.045 eV peaks, and even further around 40 meV for the 4.94 eV peak.

Under the same excitation and detection conditions, the intensities of these peaks are recorded versus the O/C content in the feeding gas. The 5.319, 5.265, 5.104 and 4.94 eV peaks have the same variations with the oxygen content in the feeding gas mixture as shown in Fig. 2. The addition of oxygen up to O/C ratio of 0.25 increases all these signals by about a factor of 4, while a further increase to O/C=0.375 brings them back near their O/C=0 values. The other peaks have a quite different behaviour. The 5.353 and 5.045 eV peaks disappear with oxygen in the feeding gas (Fig. 1), while the intensity of the 5.215 eV peak relative to the 5.265 eV peak decreases as the O/C ratio increases (Fig. 1, inset A, and Fig. 2).

Fig. 3 shows the spectrum in the energy range 4–4.76 eV for the sample with O/C=0 of the Fig. 1, but with a ×10 scale expansion. Peaks appear around 4.105, 4.256, 4.277, 4.300, 4.342, 4.383, 4.403 and 4.580 eV. Their intensities compared to that of the main 5.268 eV peak are in the range 3×10^{-3} to 5×10^{-2} while they remain very narrow with a typical full width at half maximum around 2 meV. The figure also shows a weak (10^{-3}) broad band around 4.5 eV.

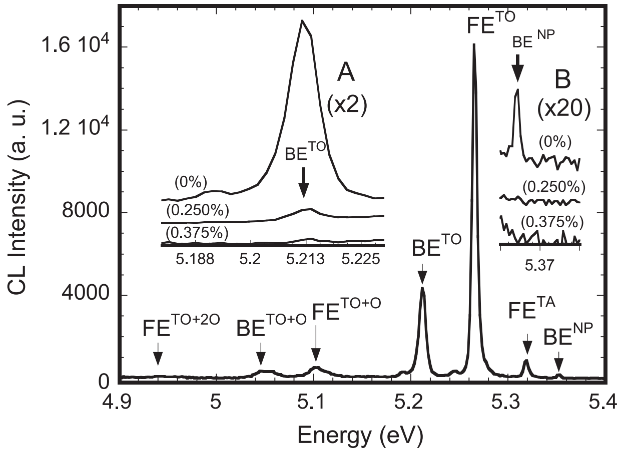

Fig. 1. Cathodoluminescence at 5 K in the exciton energy range of the film deposited with O/C=0 in the gas phase. Energy of the peaks (see Discussion): BE^{NP}, 5.353 eV; FE^{TA}, 5.319 eV; FE^{TO}, 5.265 eV; BE^{TO}, 5.212 eV; FE^{TO+O}, 5.104 eV; BE^{TO+O}, 5.045 eV; FE^{TO+2O}, 4.94 eV. After normalization on the FE^{TO} peaks. Inset A: ×2 scale expansion around the BE^{TO} peak for O/C=0, 0.25 and 0.375. Inset B: ×20 scale expansion for O/C=0, 0.25 and 0.375.

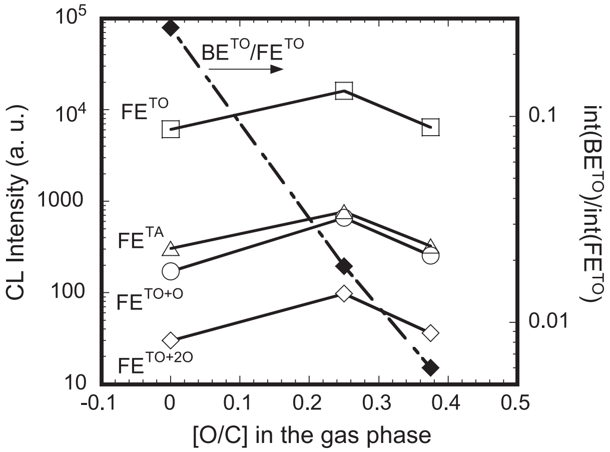

Fig. 2. Full line and right scale: For identical excitation and detection conditions, absolute intensities of the FE^{TA}: 5.319 eV; FE^{TO}: 5.265 eV; FE^{TO+O}: 5.104 eV; FE^{TO+2O}: 4.94 eV (see Discussion) peaks versus the O/C ratio in the gas phase. Dotted line and left scale: Intensity of the BETO exciton relative to the FETO exciton peak versus the O/C in the gas phase.

The variation of the intensity of the 4.105, 4.324 and 4.58 eV peaks and of the wide 4.5 eV band with the O/C ratio is qualitatively similar to that of the 5.319, 5.265, 5.104 and 4.94 eV peaks.

Curve (a) in Fig. 4 shows the spectrum of the same sample with O/C=0 in the energy range 1.8–4.2 eV. It shows narrow peaks around 2.155, 2.325, 2.462 (H3), 2.501, 3.185 and 3.771 eV, narrow bands around 2.10, 2.15, 2.22–2.27, 2.34, 2.38 and 2.42 eV and broad bands around 2.3, 2.6, 2.84 and 3.55 eV. Curves c and d of Fig. 4 show the spectra when O/C=0.25 and 0.375, respectively. As O/C increases, (i) the intensities of the narrow peaks (including H3), of the narrow bands and of the 3.5 eV band decrease and almost

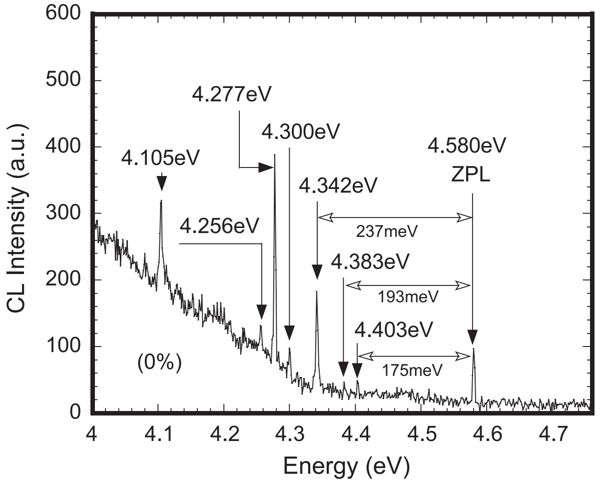

Fig. 3. Cathodoluminescence at 5 K in the 4-4.8 eV energy range of the film deposited with O/C=0 in the gas phase.

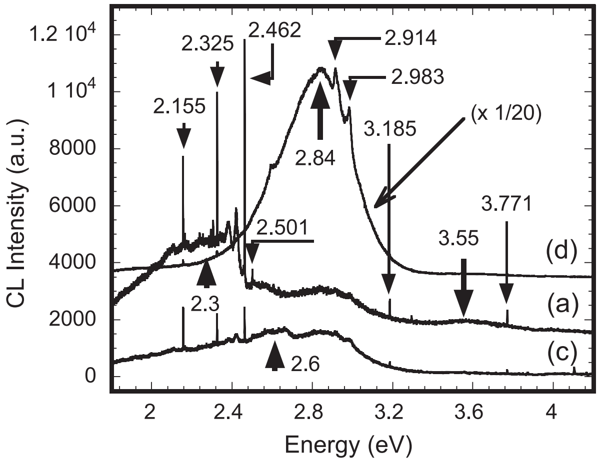

Fig. 4. Cathodoluminescence at 5 K in the 1.8-4.2 eV energy range of the film deposited with (a) O/C=0, (c) O/C=0.25, (d) O/C=0.375 in the gas phase.

disappeared for O/C=0.375. (ii) Similarly, the intensity of the 2.3 eV broad band decreases, while on the contrary, the relative intensity of 2.84 eV band increases to dominate the other broad bands for O/C=0.375 (curve d in Fig. 4) (iii) Peaks around 2.914 and 2.983 eV grow on top of the 2.84 eV broad band.

4. Discussion

The exciton peaks can be identified from the work of Dean et al. on natural and synthetic crystals [4], the Data Handbook of Zaitsev [5], the review chapter of Sauer [6]. Generally, to keep the *k*=0 selection rules, because of the indirect gap of diamond, they are associated with one or several phonons [4–6]. A first set corresponds to the recombination of the free exciton associated with a TA phonon ($\mathrm{FE}^{\mathrm{TA}}$) at 5.319 eV, a TO phonon ($\mathrm{FE}^{\mathrm{TO}}$) at 5.265 eV, a TO phonon and a O^{Γ} phonon from the centre of the Brillouin zone ($\mathrm{FE}^{\mathrm{TO+O}\Gamma}$) at 5.104 eV, a TO phonons and two phonons O^{Γ} ($\mathrm{FE}^{\mathrm{TO+2O}\Gamma}$) at 4.94 eV. The similar variations of the intensities of this set of peaks (Fig. 2) with the O/C ratio confirm this assignment.

A second set of lower intensity corresponds to the recombination of the exciton bound to the boron without phonon ($\mathrm{BE}^{\mathrm{NP}}$) at 5.353 eV, and associated with a TO phonon ($\mathrm{BE}^{\mathrm{TO}}$) at 5.213 eV, a TO and one O^{Γ} phonon ($\mathrm{BE}^{\mathrm{TO+O}\Gamma}$) at 5.045 eV.

Therefore, these non-intentionally doped (nid) films contain boron. As in the classical semiconductors [6], in the lower range of boron incorporation ($[\mathrm{B}]<5\times10^{18}$ cm^{-3}), the ratio of the intensity of the $\mathrm{BE}^{\mathrm{TO}}$ peak to that of the $\mathrm{FE}^{\mathrm{TO}}$ peak increases as the boron concentration increases in the homoepitaxial [7] and polycrystalline [8,9] diamond films. The intensity of the $\mathrm{BE}^{\mathrm{TO}}$ peak relative to that of the $\mathrm{FE}^{\mathrm{TO}}$ peak decreases from 0.27 to 6.6×10^{-3} as O/C increases from 0 to 0.375 (Fig. 2). From the work of Kasu et al. [10], these ratios correspond to concentrations of uncompensated boron decreasing from 1.6×10^{16} to 4×10^{14} cm^{-3}. Contamination by boron in the 10^{16} cm^{-3} range of homoepitaxial diamond films is usual [10]. Addition of oxygen in the feeding gas continuously decreases it down to negligible concentration of 4×10^{14} cm^{-3} when O/C=0.375. The occurrence of oxygen in the feeding gas was previously found to decrease the intentional doping level of boron in the isolated particles [11] and polycrystalline films [12] of diamond.

Quite generally, the free and bound exciton peaks widen more and more when they are associated to an increasing (from 1 to 3) to number of phonons as found here for the free (6, 22, 40 meV) and for the boron-bound (8, 24 meV) excitons in the film deposited without oxygen. The zero phonon line of boron-bound exciton ($\mathrm{BE}^{\mathrm{NP}}$) has a still lower FWHM of 4 meV. The boron might originate from the reactor walls contaminated by the previous depositions of B doped films, but also of other origins [10]. This proves that the B incorporation remains easy under the present deposition conditions, might be unavoidable in most of the deposition conditions [10], but can be controlled at least down to the 10^{14} to 10^{16} cm^{-3} ranges by suitable addition of oxygen in the feeding gas mixture.

The FWHMs of our exciton peaks compare favourably to the value obtained for the best homoepitaxial films, 5 meV for the $\mathrm{FE}^{\mathrm{TO}}$ [1,13] (when high-resolution detection is not used [6]). FWHMs of 30 meV are more usually reported [6]. From the detection of the $\mathrm{BE}^{\mathrm{NP}}$ as well as from the low FWHM values [6], we conclude that our films are of good quality.

The narrow peaks are in principle associated with point defects. First, we obtain the set of levels of the 5 RL defect (zero phonon line at 4.580 eV), ascribed to an interstitial carbon, with its 4.403 (175 meV), 4.383 (193 meV) and 4.342 (237 meV) eV classical phonon replica [5], but other peaks are detected. The other peaks also appear in the two other samples. The 4.105 eV peak might originate from the 4.580 eV zpl associated with two 237 meV phonons. The 4.256, 4.277 and 4.300 eV are not reported in Ref. [5]. As the intensities of its components follow those of the FE excitons, the 5 RL defect is unambiguously within the film. The interstitial carbon might originate [5] from an over-feeding of the film in C atoms, or from the creation of vacancies–interstitial carbon pairs under residual bombardment by ions in the centre of the plasma ball. We favour the second hypothesis.

At lower energies, the 2.155 and 3.185 eV peaks are ascribed to neutral complex defects associated with one substitutional nitrogen (Nc–Vc) and (Nc–Ic), respectively [5], while the 2.462 eV peak with its specific phonon replica (narrow bands and the 2.325 eV peak) is associated with the H3 centre (Nc–Vc–Nc). The 2.501 eV peak is specific to CVD diamond films [6], while the 3.771, 4.256, 4.277 and 4.300 eV peaks were not reported previously [5,6]. Their intensities also decrease when the O/C ratio increases.

Therefore, there is some contamination of the films by nitrogen although it is expected to be low because of the low intensity of these peaks relative to that of the FE^{TO}. It decreases as the O/C ratio in the gas phase increases.

On the contrary, the intensity of the 2.98 eV peak—ascribed to the N3 centre [5] (with its phonon replica at 2.91 eV), three substitutional nitrogen associated with a carbon vacancy—grows as O/C increases. This suggests that increasing the O/C ratio strongly modifies the nature of the defects associated with residual nitrogen, Nc–Vc, Nc–Ic, H3 associated with one or two nitrogen atoms being gradually replaced by N3 defect involving three nitrogen atoms.

Quite generally, the broad bands originate from extended defects in the diamond films. The well-known 2.84 eV (A band) is now associated to dislocations and/or planar defects [1]. The 2.3 eV band appears in boron-doped polycrystalline [9] and homoepitaxial [7] diamond films. It is ascribed to donor (nitrogen)–acceptor (boron) pairs decorating dislocations [9,6]. As the O/C ratio increases, the boron and the nitrogen concentrations decrease, in agreement with the decrease of the 2.3 eV band while the 2.84 eV band increases. Similar opposite variations of the intensities of the 2.3 and 2.84 eV bands as the boron concentration increases were previously reported for polycrystalline films [9,6].

The 2.6, 3.55 and 4.5 eV broad bands were previously found in the CL spectra of slightly boron doped homoepitaxial diamond films [14]. They are associated with boron. The 3.6 and 4.6 eV bands were also found in the CL spectra of various boron doped diamond samples [15,6], and in the electroluminescence spectra of homoepitaxial (111) p–n junctions [16]. The decreasing intensity of these peaks and of the boron content as the O/C ratio increases is consistent with such assignments. However, their physical origin remains unclear [15,6].

The maximum intensity of the free exciton peaks for O/C around 0.25 (Fig. 2) can be understood from these opposite variations of the concentrations of the various defects as O/C increases. A maximum in the FE^{TO} signal of polycrystalline films for a specific oxygen concentration in the plasma was also found by Kawarada et al. [2].

5. Conclusions

This work shows the effect of adding oxygen to the feeding gas on the various residual defects and on the free and boron-bound excitons of nid epitaxial {100} diamond films deposited at the centre of the plasma ball.

There is some B (1.6×10^{16} cm^{-3}) and N contamination of the films, but the occurrence of BE^{NP} exciton peak and the low FWHM of their exciton peaks prove their good quality. As the O/C ratio in the gas phase increases, (i) the intensities of the Nc–Vc, H3, Nc–Ic peaks and of the 2.3 eV broad band decrease, together with the nitrogen incorporation. (ii) The intensity of the peak from the N3 defects increases. (iii) The relative intensity of the boron-bound exciton peak decreases along with the boron incorporation down to 4×10^{14} cm^{-3}, (iv) and the 2.8 eV (A) band appears with a growing intensity.

These opposite variations of the radiative defects concentrations as O/C increases result in a maximum of the free exciton signals for O/C around 0.25. The 5 RL peaks from interstitial carbon have a similar variation with O/C.

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