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# Study of the phosphorus incorporation in n-doped diamond films by cathodoluminescence

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## Abstract

The incorporation of phosphorus (P) dopants as donor atoms in chemical vapour deposition (CVD) diamond is studied by cathodoluminescence (CL). P-doped and undoped samples with identical CVD growth conditions are analysed. Variations in the spectral emission of the doped diamond are observed depending on the orientation of growth sectors. Indeed, strain relaxation through crack generation induces the formation of a faceted topography of the substrate surface. Centres associated with P incorporation seem to be responsible for the change in the CL spectral emission in the non-(111) facets. This indicates that n-type diamond can probably be grown on other than (111) orientation. Excitonic emission from liquid He to room temperature is observed for both samples as a result of the high quality n-doped growth.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Wide bandgap materials have recently attracted the interest of the scientific community for new applications such as optical emission in the visible/UV range, high power related devices and even micro-electromechanical/nano-electromechanical systems (MEMS, NEMS). Among the different large bandgap materials, diamond is one of the most promising. Its chemical inertness makes it very attractive for biological applications or for devices exposed to very aggressive environments in terms of chemical activity, high pressure, radiation or high temperatures. The very large bandgap (5.47 eV at room temperature) opens the way to solar blind UV detectors or UV emitting devices. However, the major technological limitations of this material for applications requiring a p–n junction are related to the difficulty in obtaining n-doped epitaxial layers. The first is overcome by the incorporation of phosphorus during CVD growth or by ion implantation [1, 2]. However, the incorporation of P atoms only on (111) oriented facets with its subsequent polishing difficulties, the ability of H atoms to passivate the P donors and the high dependence of P incorporation on the growth conditions make it very difficult to obtain high quality n-type films [3, 4]. The second limitation is surprisingly the tensile state of the CVD grown diamond layer on (111) oriented diamond substrates. This is still an open question despite specific studies carried out [5].

In this contribution, n-doped diamond films are studied by cathodoluminescence (CL) from 5 K to room temperatures in a planar view orientation. As a reference sample, an undoped film (labelled sample 68) has been grown under identical experimental conditions to demonstrate the effect of the P incorporation into the diamond lattice by comparing it with other n-doped samples. Here, results of only one of them (labelled sample 66) are reported, showing a representative behaviour of the n-type samples. The samples are grown by CVD on $\langle 111\rangle$ oriented synthetic substrates using the microwave plasma technique to allow atomic deposition. The $PH_3$ and $CH_4$ gas concentrations used are 0.05% that of $H_2$ and the growth temperature is 880 °C. The donor density is estimated by Hall measurements to be in the $10^{18}$ $cm^{-3}$ range. The CVD film thickness is estimated to be around 10 $\mu$m for both samples.

## 2. Results and discussion

Figure 1 shows CL spectra obtained on samples 68 and 66 at liquid helium temperature. For the doped sample, spectra are recorded from region 1 (see the scanning electron microscope (SEM) micrograph of figure 1(c)) near the edge at three different locations. Changes in the relative intensity of the peaks indicate a non-uniformity of the dopant incorporation. Indeed, as observed by other authors [6, 7], P incorporation induces bound exciton luminescence with a transverse optical phonon replica related peak at 5.175 eV. This peak intensity and energy with respect to the well known free exciton (also known as the TO phonon replica) related peak ($FE^{TO}$) at 5.269 eV indicates local variations in the P incorporation. Free and bound exciton recombinations with 2TO replicas are also observed at 5.112 eV (sample 68) and 5.023 eV (weak on sample 66), respectively. This means that the energies ($E_{TO}$) of the transverse optical phonon involved are 157 and 154 meV. This value is close to that reported elsewhere [6, 7]. The main feature of these results is the strong change of the CL spectra when P is incorporated in the diamond lattice as an n-type dopant. The competition between free and bound excitons is responsible for the decrease of the $FE^{TO}$ band and for the increase of the $BE^{TO}$ band. Moreover, the other free exciton replica, $FE^{TA}$ (at 5.325 eV, transverse acoustic replica), and the $FE^{2TO}$ (at 5.112 eV) are not always observed in the doped sample. Only in some places of region 1 can those excitonic recombinations (spectra figure 1(b)) be recorded. In addition, other recombinations can be observed such as the 5.240 and 5.211 eV peaks. A similar behaviour has not been reported in the literature. The only other features that have been observed previously are the D1-type lines (acceptor bound excitons, LO replica) [8].

In the major part of all analysed n-doped samples, a peak at 5.127 eV (241.8 nm) is found to dominate the bound-exciton luminescence (see, for example, figures 2(b) and 3(a): note that the peak energy change due to the difference in sample temperature). This peak never appears in undoped samples and has been reported only in some cases of n-doped samples. In figures 1(b) and 2(a) it is detected as a simple shoulder of the main 5.175 eV (at $T = 5$ K) bound-exciton peak. Both peaks clearly compete in the carrier recombination. When the first $BE^{TO}$ saturates (see figure 2(a)) at high injection levels, the 5.135 eV peak increases. The latter have been previously observed by other authors [2] and ascribed to a P-related defect centre interacting with TO phonons [7]. The behaviour of this line with respect to the carrier injection and temperature (observed from 5 K to room temperature as shown in figure 2(b), where the three main excitonic recombination channels are active) seems to indicate an excitonic nature

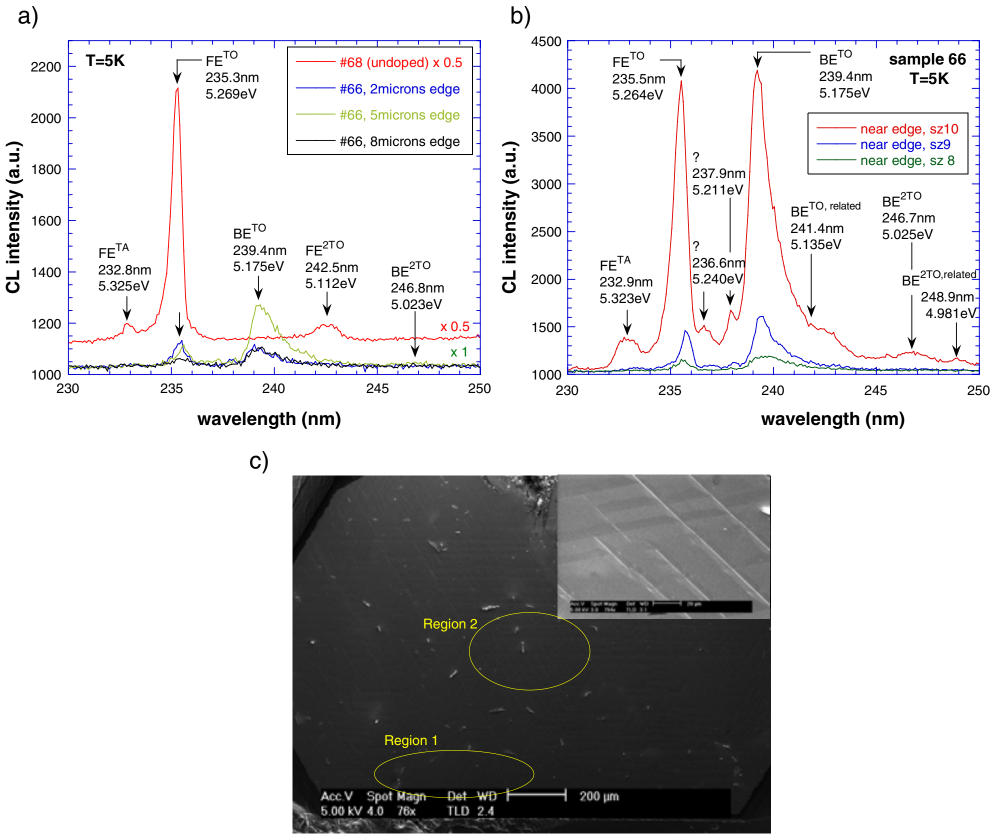

**Figure 1.** (a) Liquid helium temperature CL spectra of samples 68 and 66 recorded in region 1 of the SEM micrograph. The spectra corresponding to sample 66 are obtained at 2, 5 and 8 $\mu$m from the edge of the sample. (b) Spectra obtained from a different location (refer to figure 1(a)) in region 1 for different injection levels (sz means spot size and corresponds then to different beam currents). (c) SEM in secondary electron mode (SE) showing the topography of sample 66 in regions 1 and 2. Note the facets observed on the whole surface but with a higher density in region 2. The inset of figure 1(c) shows a faceted region.

of this recombination peak. Assuming a donor binding energy of 90 meV for the P atoms, this associated centre should have a binding energy value around 130 meV. An analysis of its line intensity, with respect to the temperature, should determine the corresponding centre binding energy by fitting this intensity to an Arrhenius curve. Such studies are in progress.

Finally, as shown in figure 3, no correlation between this recombination centre and cracks, generated by the lattice strain relaxation, are observed. Spectra recorded at different locations with respect to one crack do not show any change in energy, indicating that the 5.135 eV line does not result directly from strain or defect generation. However, as the observed crack corresponds to region 2 (inset of figure 1(c): between facets, cracks have been observed) and since the appearance of the 5.135 eV band seems to be related to the presence of facets (region 1 shows a much lower facet density than region 2), we attribute the generation of this centre to growth on non-(111) surfaces. It is only very recently that P incorporation has been reported to be possible on other than (111) surfaces during epitaxial growth [9]. Indeed, {011} and {113} oriented sectors are reported to be very efficient in FE emission. A similar behaviour of bound

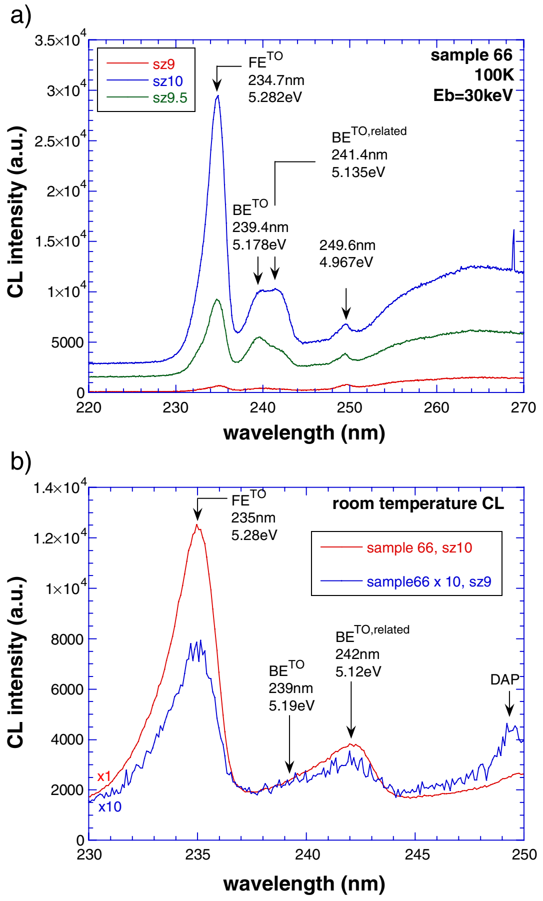

**Figure 2.** CL spectra from region 1 at higher temperatures and different injection levels. (a) Saturation of the $BE^{TO}$ peak is obvious and (b) the presence up to room temperature of the three $FE^{TO}$, $BE^{TO}$ and $BE^{TO,related}$ peaks is shown with a predominance of the last one. Note that sz means spot size and corresponds then to different beam currents, with sz9 corresponding to a lower beam current than sz10.

excitons to that reported here was shown, where the appearance of the 5.135 eV peak kills the FE emission. Kanda *et al* ascribe this peak emission to a shift of the $BE^{TO}$ emission (as a result of a defective region). We demonstrate here that this is not the case: figure 2(a) shows that both emissions can persist in the same e-beam location. It seems clear that this peak belongs to another donor level. It is not due to a strain-induced shift of the bound exciton energy luminescence. However, this behaviour seems to indicate that P incorporation is also possible in vicinal orientation as shown in figure 1(c), the SEM micrograph inset. Further atomic force microscopy $C/V$ profiles and mapping should confirm the P donor character in those vicinal orientations.

## 3. Conclusion

A CL study of undoped and phosphorus doped (111) CVD diamond is reported. In addition to the well known excitonic recombinations observed in such material, a new line is reported

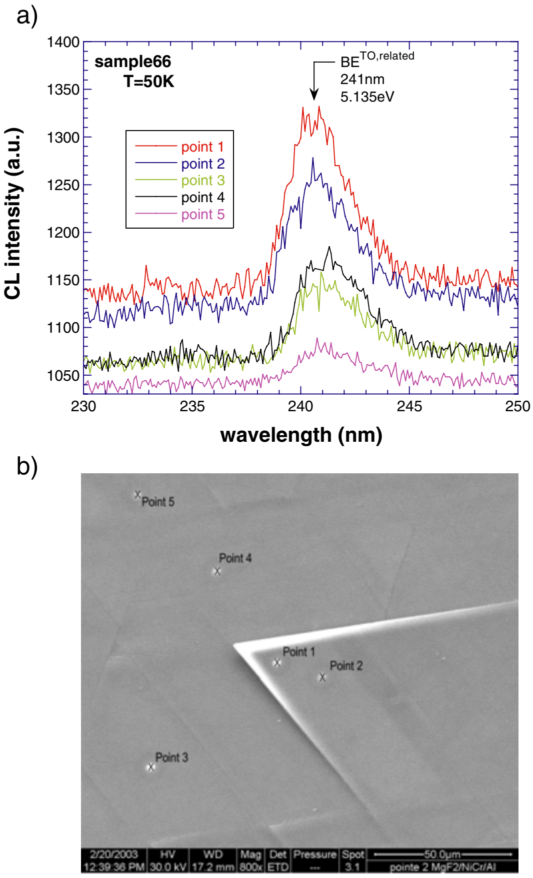

**Figure 3.** (a) Several CL spectra recorded at 50 K near a crack, (b) evidence of the non-dependence energy of the 5.135 eV peak to strain or defect generation.

at 5.135 eV and is tentatively attributed to bound exciton to donor recombinations involving TO phonons. The involved centre seems to be induced by the presence of phosphorus in the diamond lattice and is related to regions where growth vicinal to (111) facets occurs. This seems to indicate that P incorporation in diamond growth is also possible in other orientations than (111). The FE$^{TO}$, BE$^{TO}$ and the 5.135 eV (BE$^{TO,related}$) peaks are observed from 5 K to room temperature, indicating a good quality of the CVD grown samples.

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