

# Ionoluminescence in CVD diamond

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## I. INTRODUCTION

IBIL (Ion Beam Induced Luminescence) is a very powerful technique [1] for material investigation. With respect to photoluminescence, it presents the big advantage of full excitation of all the existing radiative centres and of a complete control of the emission region, which is given by the range of ions and by the scanned surface area, whereas with respect to cathodoluminescence, it is a real bulk technique. It has a much larger signal-to-noise ratio, it can work in a time-resolved approach and measure the local radiative lifetime of carriers and it can also be coupled on the same apparatus with a much more sensitive technique for detection and mapping of trace elements such as PIXE ( Particle Induced X-ray Emission ).

By the new IBIL apparatus at the Laboratori Nazionali di Legnaro (LNL), a series of measurements concerning both wide area luminescence spectra and monochromatic luminescence maps with few micrometers space resolution have been carried out on several CVD diamond samples [2]. Two MeV protons with a penetration depth of about 25 micrometers have been used in order to investigate the materials in the bulk. These measurements have been correlated with PIXE (Particle Induced X-Ray Emission) and ESR (Electron Spin Resonance). The measurements have been performed at increasing proton doses in order also to investigate the radiation hardness of luminescence peaks.

The results indicate that ionoluminescence of CVD diamond is dominated by three bands around 2 (E1), 2.4 (E2) and 2.9 (E3) eV, the intermediate one being very radiation hard and the other two radiation weak. The band at 2 eV is correlated with N content and it is particularly high in samples with poor electronic properties.

## II. EXPERIMENTAL SET-UP

Ionoluminescence data were obtained by a new version of the IBIL apparatus [1], which allows for an almost  $2\pi$  solid angle for light collection, with a light transport outside of the scattering chamber, by a vacuum light pipe which does not introduce absorption even at the highest or at the lowest wavelengths and a standard 0.25 m Jobin-Yvon monochromator and a wide spectral range phototube. The proton or ion beam hits the sample after crossing a hole in the metal mirror (1 mm of diameter).

The signal from the photomultiplier is recorded using a standard amplification chain. When the microbeam is in a certain position, a gate is open (about 70  $\mu$ s duration) to allow pulses to be collected through the amplification chain until the beam moves to the next position. The (x, y) coordinates of the beam are recorded together with the number of pulses. The scan area in the present case is 0.5 x 0.5 mm<sup>2</sup> and the scan time, for a map of 512 x 512 pixels, is of the order of 18 s. Several minutes are needed in order to get a good map, depending on the radiative efficiency of the sample. When an IBIL map is not needed, by defocusing the microbeam it is possible to work with a relatively wide beam of dimensions comparable with the scan area, in order to get simply average IBIL spectra as a function of wavelength by the automatic scan of the monochromator and by collecting and amplifying the output current from the phototube. Beam current intensities are generally of the order of 100 pA in order to have a good signal. Together with IBIL, it is possible to get PIXE maps by collecting X-ray pulses due to protons with a Si(Li) detector placed in the same scattering chamber as in EDAX (Energy Dispersive Analysis by X-Ray) in standard SEM microscopes, with the advantage of a much better sensitivity because of absence of bremsstrahlung background.

The investigated samples were CVD diamond polycrystals with dimensions of about (1x1x0.04) cm<sup>3</sup>.

## III. RESULTS

Fig. 1 shows several IBIL spectra carried out over the diamond samples CM1 and R117 in subsequent time intervals. The E3 (430 nm) peak in sample CM1 is usually attributed to the A band and progressively disappears with time and proton dose, as shown in Fig. 2. IBIL maps, not shown here, indicate not only that A band is not homogeneously distributed in CVD diamond, but also that the different wavelengths included in the A band, from 400 to 460 nm, display exactly the same spatial distribution, with the conclusion that the blue A-band could be attributed to the same radiative center which can have different configurations, or to the same cluster of correlated or compensated defects.

The E2 (510 nm) peak is almost constant as a function of the proton dose and is attributed to the center H3 created by the radiation damage. Both the E2 and E3 peaks were already detected in CVD samples of good electronic

quality.

Since a very good spatial correlation was found also in our case between the bidimensional maps of the two centers, it is quite obvious to attribute the blue A band to N

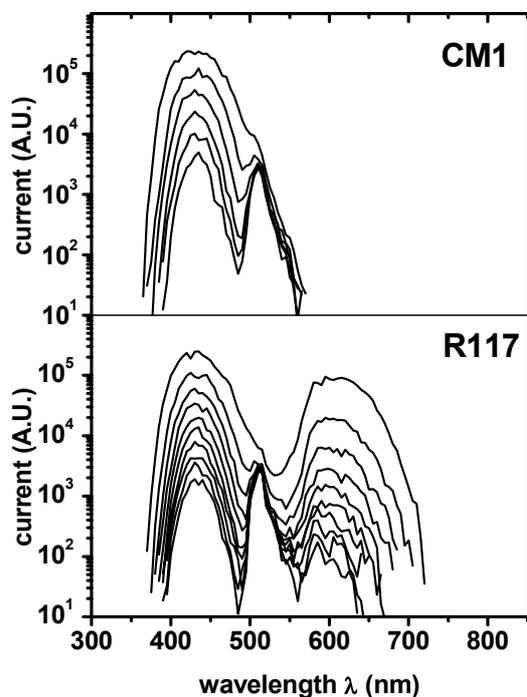


Fig. 1 - IBIL spectra of CVD diamond samples CM1 and R117 as recorded at increasing times. IBIL intensity continuously decreases. Each spectrum corresponds to about  $10^{15}$  p/cm<sup>2</sup> of proton dose over a surface area of  $0.5 \times 0.5$  mm<sup>2</sup>. Sample R117 is characterized by a poorer charge carrier collection efficiency with respect to the sample CM1.

-N defects which decorate the grain boundaries and the other band, which is also called green A band, to N - V - N defects locally created by protons themselves. In fact, protons, which create vacancies in concentration of at least  $10^{19}$  cm<sup>-3</sup>, can produce vacancies also in the damaged regions and close to these N-related defects, giving rise to the green A band at 510 nm. This band, once created, does not seem to be sensitive to damage.

Similar spectra were obtained for sample R117 except for the appearance of a large band (E1) in the 580 - 630 nm interval. PIXE measurements were unable to detect any kind of impurity in CVD diamond samples for atomic numbers below  $Z = 11$  (Na).

ESR analysis show in sample R117 a nitrogen concentration larger than 1 ppm, whereas in sample CM1 the nitrogen concentration was much lower.

Other measurements carried out on different samples confirm a correlation, between the area under the peak E1 and the N content, whereas it seems that the area under the

peak E3 at 430 nm is greater when N concentration is lower or below 1 ppm.

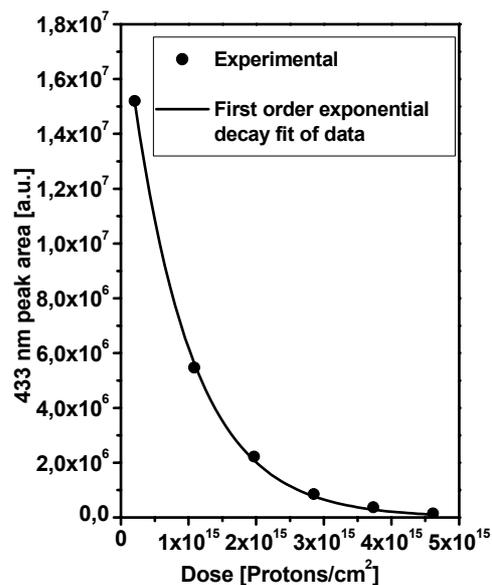


Fig. 2 - Decay of the A band intensity as a function of proton dose. The intensity has been calculated as the total area under the peak at 430 nm.

The band at 2 eV (E1) which is very sensitive to the radiation damage, was not previously detected [3] in IBIL measurements, but it can be tentatively attributed to a N - V complex dispersed in the grains, since it is present only in samples in which the charge collection efficiency is very low and much less than grain dimensions. In fact, it is reasonable to state that when nitrogen is used in order to increase the growth rate above certain limits, nitrogen could be no more capable to segregate at the grain boundaries and it may appear in the bulk of the grains, limiting further the charge collection length.

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