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Ionoluminescence in CVD diamond and in cubic boron nitride

C. Manfredotti^{a,*}, E. Vittone^a, A. Lo Giudice^a, C. Paolini^a, F. Fizzotti^a, G. Dinca^b, V. Ralchenko^c, S.V. Nistor^d

^a Experimental Physics Department, University of Torino, and UdR Torino University of INFM, Torino, Italy ^bDacia Synthetic Diamond Co., Bucharest, Romania ^c General Physics Institute, Russian Academy of Sciences, Moscow, Russia ^dNational Institute for Materials Physics, Magurele-Bucharest, Romania

Abstract

Using the new ion beam-induced luminescence (IBIL) apparatus in National Legnaro Laboratories, Italy, a series of measurements concerning both wide-area luminescence spectra and monochromatic luminescence maps with a space resolution of a few μ m has been carried out on several CVD diamond and c-BN samples. Protons of 2 MeV with a penetration depth of approximately 25 μ m have been used in order to investigate the materials in the bulk. These measurements have been correlated with particle-induced X-ray emission (PIXE) and EPR data. The measurements have been performed at increasing proton doses in order to also investigate the radiation hardness of luminescence peaks. The results indicate that ionoluminescence of CVD diamond is dominated by three bands at approximately 2, 2.4 and 2.9 eV, with the intermediate band being very radiation-hard, and the other two radiation-weak. The band at 2 eV is correlated with N content, and is particularly high in samples with poor electronic properties. IBIL in c-BN is also dominated by three bands, one at approximately 2 eV, and the other two at higher energies with respect to CVD diamond. All these three bands seem to be relatively radiation-hard with respect to CVD diamond, and to be related to defects induced by doping. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Ion beam-induced luminescence (IBIL) is a very powerful technique [1-5] for material investigation by looking at radiative recombination centers. With respect to photoluminescence, it has the big advantage of full excitation of all the existing radiative centers and of a complete control of the emission region, which is given by the range of ions and by the scanned surface area, while, with respect to cathodoluminescence, it is a real bulk technique. It has a much larger signal-to-noise ratio, can operate in a time-resolved regime and measure the local radiative lifetime of carriers, and can also be coupled with a much more sensitive technique for detection and mapping of trace elements, such as particle-induced X-ray emission (PIXE), on the same apparatus.

Moreover, IBIL has been used in the recent past [6-8] together with ion beam-induced current or charge (IBIC) in order to investigate the radiative or non-radiative nature of centers which lower the performance of detectors (nuclear, light) built with new materials, such as CVD diamond.

Until now, the IBIL apparatus at Legnaro Laboratories (Italy) has been used in a panchromatic mode in a

^{*}Corresponding author. Tel.: +39-011-6707306; fax: +39-011-6691104.

E-mail address: manfredotti@to.infn.it (C. Manfredotti).



Fig. 1. Layout of the ionoluminescence apparatus in Legnaro Laboratories (Italy). The hole in the mirror has a diameter of 1 mm, while the diameter of the beam is 2 μ m.

microbeam line of the 2.5-MeV electrostatic accelerator, with a coincident set-up in order to improve the signal-to-noise ratio.

2. Experimental

In this work, results are presented which have been obtained by a completely new version of the apparatus, as shown in Fig. 1, which allows for an almost 2π solid angle for light collection, with light transport outside of the scattering chamber by a vacuum light-pipe, which does not introduce absorption, even at the highest or lowest wavelengths, 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 in diameter). The signal from the phototube is recorded using a standard amplification chain. When the microbeam is in a certain position, a gate is open (approx. 70 µs duration) to allow the collection of pulses through the amplification chain until the beam moves to the next position. The (x,y) co-ordinates of the beam are recorded, together with the number of pulses. The scan area in the present case is 0.5×0.5 mm², and the scan time, for a map of 512×512 pixels, is of the order of 18 s. Several minutes are needed in order to obtain a good map, depending on the radiative efficiency of the sample. Maps at a certain wavelength can also be carried out by using interference filters instead of the monochromator. When an IBIL map is not needed, it is possible to work with a relatively wide beam, of dimensions comparable with the scan area, by defocusing the microbeam. This yields simple average IBIL spectra as a function of wavelength using 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 700-800 pA to obtain a good signal. Together with IBIL, it is possible

to use PIXE by collecting X-ray pulses due to protons with a Si(Li) detector placed in the same scattering chamber as in energy dispersive analysis by X-ray (EDAX) in standard SEM microscopes, with the advantage of a much better sensitivity because of the absence of Bremsstrahlung background.

The samples investigated were CVD diamond polycrystals with dimensions of approximately $1 \times 1 \text{ cm}^2 \times 400 \mu \text{m}$, or c-BN sintered powders in platelets of comparable dimensions.

3. Results: CVD diamond

Fig. 2 shows several IBIL spectra carried on the diamond sample CM1 over subsequent time intervals. The blue A-band at 430 nm progressively disappears with time and proton dose, while the green A-band at 510 nm is almost constant as a function of the proton dose. IBIL maps, not shown in this work, indicate that, not only is the A-band not homogeneously distributed in CVD diamond, but also that the different wave-



Fig. 2. IBIL spectra of CVD diamond sample CM1 as recorded at increasing times. IBIL intensity continuously decreases. Each spectrum corresponds to approximately 10^{15} p/cm² of proton dose over a surface area of 0.5×0.5 mm².



Fig. 3. IBIL spectra of CVD diamond sample R117 as recorded at increasing times under the same conditions as in Fig. 2. Sample R117 is characterized by a much poorer charge carrier-collection efficiency with respect to sample CM1.

lengths 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.

Fig. 3 shows several IBIL spectra as in Fig. 2, carried out on a different CVD diamond sample, R117: the spectra are very similar, except for the appearance of a large band in the 580–630 nm interval. Sample R117 is characterized by a larger N content, very poor detector performance, and very short charge-collection lengths.

Fig. 4 shows the decay curve of IBIL intensity of the A-band, simply evaluated from the area of the peak, as a function of proton dose: it is exponential. This observation could be explained only by an enhancement of the process of center destruction or removal, produced directly by the actual destruction or removal of centers.

PIXE measurements were unable to detect any kind of impurity in CVD diamond samples for atomic numbers below Z = 11 (Na). Nitrogen could not be detected because of the low energy of characteristic Xrays, but it is certainly present, at least at ppm level, as indicated by the EPR data. In fact, Table 1 reports the energies of the three ionoluminescence peaks, together



Fig. 4. 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.

with the concentration of N as detected by ESR measurements, and the areas under peaks E1 and E3. There is an evident correlation, although not quantitative, between the area under the E1 peak and the N content, while it seems that the area under the peak E3 is greater when the N concentration is below 1 ppm, but these arguments are left for the discussion.

4. Results: c-BN

Fig. 5 shows the IBIL spectra of a c-BN sample



Fig. 5. IBIL spectra of c-BN sample CBN2 taken at increasing times and proton doses, in the same way as in Fig. 2. Sample CBN2 is strongly doped with Mg during growth.

Table 1

Peak energies of the three ionoluminescence bands recorded in CVD diamond, together with N concentration as detected by ESR and the areas of peaks E3 and E1

nple	E1 (eV)	E2 (eV)	E3 (eV)	ESR N conc. (ppm)	Peak E3 area (A.U.)	Peak E1 area (A.U.)
5	1.98	_	2.91	12	1.13	50.3
17	2.03	2.43	2.87	1.5	14.3	70.6
130	2.06	2.42	2.86	1.5	14.1	0.26
[1	-	2.48	2.89	< 1	15.3	-
[3	-	2.48	2.85	< 1	45.7	-
UC	-	2.46	2.87	< 1	42.6	-
UV	-	2.46	2.93	< 1	36.6	-
UV	-	2.46	2.93	< 1	36.6	



Fig. 6. IBIL spectra of c-BN sample CBN7 taken at increasing times and proton doses. Sample CBN7 is strongly doped with Ca.

intentionally doped with Mg. As in the previous case, the spectra were also taken at increasing proton doses, but they do not seem to be influenced as much by radiation dose (IBIL intensity is now linear in the vertical scale). Three bands are evident.

Fig. 6 shows similar spectra taken for another c-BN sample intentionally doped with Ca: they are not dramatically different from Fig. 5, except for different relative heights of the peaks and for the appearance of a new peak at 700 nm. In fact, reconstruction of the peaks simply carried out by a Gaussian fit (see Fig. 7) indicates that the peaks have the same positions, but different heights, except perhaps at the longest wavelengths.

An overview of the ionoluminescence peaks revealed in c-BN is reported in Table 2, together with the precursor used in the growth of the samples and their apparent color. The positions and areas under the peaks were calculated by fitting the spectra, transformed as a function of energy, with Gaussian curves. It is clear that peak E1 appears only in samples doped with Ca, while the E3 peak is present in all the samples, with fluctuations in the area under the peak much less important with respect to the other three peaks. Since these fluctuations have some correlations with the fluctuations in the beam intensity during the measurements, we shall use this peak in order to normalize the others, with the aim of finding correlations between Ca and Mg content and the peak area.



Fig. 7. Reconstruction of IBIL peaks of samples CBN2 and CBN7.

5. Discussion

The most striking feature of the results is connected with the apparent high radiation resistance of c-BN, as measured on the ionoluminescence peaks, with respect to CVD diamond. This could be attributed to the absence of grain boundaries in c-BN, the c-BN samples being essentially assemblies of monocrystals (with dimensions between 20 and 40 μ m) without the highly strained regions present at the grain boundaries of CVD diamond. Another feature is also represented by the differing roles of N in CVD diamond (in which it is a natural dopant, probably improving the growth rate and stabilizing a material that is relatively unstable by itself) and in c-BN (in which N belongs to the lattice).

Pointing towards a tentative attribution of the IBIL peaks, the first observation to be made in Table 1 is that the E1 peak is present in only three of the six CVD diamond samples. In order to interpret this, we should remember that samples with a larger N content display shorter charge-collection lengths or poorer electronic properties in terms of lifetime and mobility of carriers. Peaks E3 and E2 were already detected in CVD samples of good electronic quality [7,8] and were

Table 2

Peak energies of the four ionoluminescence bands recorded in c-BN, together with precursor used in preparation, and color of the samples

Sample	Precursor	Color	E1 (eV)	E2 (eV)	E3 (eV)	E4 (eV)
CBN1	Mg	Black	_	1.92	3.32	3.83
CBN2	Mg	Black	_	1.93	3.33	3.87
CBN3	$Mg_2N_2 + NH_4F$	White	-	1.93	3.33	3.85
CBN4	$Ca_3N_2 + LiF$	Amber	1.61	1.9	3.24	3.93
CBN5	$Ca_3N_2 + LiF$	Amber	1.68	1.95	3.14	3.89
CBN6	$Ca_3N_2 + LiF$	Amber	_	1.91	3.14	-
CBN7	$Ca_3N_2 + LiF$	Amber	1.75	2.05	3.14	3.82

attributed to the blue A-band and the H3 center created by radiation damage, respectively. Since a very good spatial correlation between the bidimensional maps of the two centers was also found in our case, it is quite obvious to attribute the blue A-band to N–N defects, which decorate the grain boundaries, and the other band, which is also called the green A-band, to N–V–N defects, created locally by protons themselves. In fact, protons, which create vacancies in concentration of at least 10^{19} cm⁻³ according to our estimates, can also produce vacancies (and more likely) 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.

The band at 2 eV (E1) was not previously detected [2,3] 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 the 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 may no longer be capable of segregating at the grain boundaries and it may appear in the bulk of the grains, further limiting the charge-collection length. It is worthwhile to note that the E1 peak is also very sensitive to radiation damage.

In the case of c-BN, the approach taken in the CVD diamond case cannot be used, since in our case, c-BN samples had no grain boundaries, and also because N atoms belong to the lattice and do not represent points for the easier creation of vacancies.

The structure and the chemical composition of c-BN seem to be favorable for a better resistance to radiation damage, as seen in IBIL data. This fact, coupled with the observation that ionoluminescence of c-BN is very high, even with respect to CVD diamond, could indicate a good possibility for applications of c-BN in extreme radiation environments (thermoluminescent dosimetry, for instance). Looking at the IBIL spectra, the first observation is that there is a good similarity between samples CBN1, CBN2 and CBN3 on one side, and between all the other samples on the other side. Since in the former case the similarity is given more directly by the shape of the first two peaks (E1 and E2), it would be obvious to try to attribute them to Mg or to Mg-created defects. In the latter case, the similarity is better given by the last peak, E4, so we tentatively attribute it to Ca or Ca-induced defects.

A demonstration of the reasonability of our attributions is shown in Fig. 8, which displays the areas under the E1and E2 peaks as a function of Ca content as detected by PIXE, and in Fig. 9, which displays the area under the E4 peak as a function of Mg content. A correlation is quite evident in both cases, even for a sample like CBN3, which displays a different color and



Fig. 8. Plot of the total area of peaks E1 and E2 (see Table 2) as a function of Ca content in ppm, as detected by PIXE.

which was grown with a quite different precursor. Only CBN4 in Fig. 8 and both CBN7 and the same CBN4 in Fig. 9 are not correlated with Ca and Mg content, respectively; in fact, their contribution was not included in the fit. We have no explanation for this, and we also have no way to include possible effects of the observed color of the sample on the IBIL spectra. However, the correlation does exist for most of the samples, even if it cannot be put forward as a proof of our attributions.

6. Conclusions

It has been demonstrated, by IBIL spectra and maps, that a correlation does exist between the electronic properties and the band at 2 eV in CVD diamond, which can be taken as an indication of poor charge-collection properties. Ionoluminescence is not uniformly distributed, and at least the blue A-band seems to be correlated with grain boundaries. The presence of the A-band is not to be taken as a proof of disorder, which does exist anyhow in grain boundaries, but more likely to some kind of passivation or decoration carried out



Fig. 9. Plot of the total area of peak E4 (see Table 2) as a function of Mg content in ppm, as detected by PIXE.

by nitrogen at the grain boundaries. The collection length is, in any case, limited by trapping or recombination at the grain boundaries. When an excess of nitrogen is introduced into a CVD diamond sample, it likely also induces defects in the grains, with the consequence of a further limit to the charge-collection length. In fact, it has been recognized that charge-collection length distribution in CVD diamond is characterized by two peaks, and that only the peak at the lower collection lengths moves with the bias voltage, with the other one fixed by the dimensions of the grains [4].

c-BN is a very good luminescent material, characterized by four luminescence bands with intensities which seem to be quantitatively connected to the kind of doping. In contrast with diamond, and at least in our samples, ionoluminescence originates from the bulk of the material. PIXE and IBIL maps will also be carried out on polycrystalline samples of c-BN in order to understand better the origin of the ionoluminescence.

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