Thermoluminescence properties of high-dose gamma-irradiated diamond films

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Abstract. Thermoluminescence (TL) properties of gamma-irradiated chemical vapor deposition (CVD) diamond films at high doses are presented. Samples of undoped and nitrogen-doped CVD diamonds were exposed to 60Co gamma sources and TL intensity as a function of the dose was analyzed. To evaluate the feasibility of using these materials as TL high-dose dosimeters, reproducibility of the TL signal, and the TL response as a function of absorbed dose from 100 Gy up to 10 kGy were studied. Furthermore, the fading of the TL glow curve was analyzed. Finally, to estimate the kinetics parameter values associated with the trap distribution in the CVD diamond, a computerized deconvolution was carried out by using the general order kinetics (GOK) model.

1. Introduction
In the last years, chemical vapor deposition (CVD) diamond has been studied as a prospect material for dosimetry in biomedical applications due mainly to diamond is a near tissue-equivalent material (Z\textsubscript{eff} ≈ 6) \cite{1} and its non-toxicity \cite{2,3}. Besides, it is chemically inert and highly resistant to high radiation doses, keeping the same TL response after successive cycles of irradiation, heating and readout. In particular, TL characteristics like sensitivity, dose dependence, fading, and the linearity dose-response of CVD diamond films have been investigated for dosimetry applications \cite{4-7} but in all cases, the luminescence properties have been reported only for low doses, namely, from 10-2 Gy up to 10 Gy. Also for high doses, it has been found a saturation in the TL glow curve of CVD diamond for doses higher than 500 Gy \cite{7-9}. On the other hand, it is well known that the TL performance of CVD diamond depends on the impurities concentration and doping materials introduced during the growth of the samples \cite{10,11}. Nitrogen is frequently present in the diamond samples due to the gas flux used during growth-producing intrinsic defects. It was found that the nitrogen-doped samples exhibited a TL glow peak at about 250°C in the single CVD crystal diamond \cite{7}. Consider these facts, it was doped CVD diamonds with 750 ppm of nitrogen and studied the TL properties of these
compounds at high doses. This paper aimed to report the results of gamma-irradiated CVD diamond films for high-dose gamma radiation.

It has been studied the reproducibility of the TL signal, the dose-response from 700 up to 10 kGy, and the fading of the TL glow curve for undoped and 750 ppm nitrogen-doped microwave chemical vapor deposition (MWCVD) diamond films. According to the obtained results, it is possible to use these materials as high dose TL detectors.

2. Experimental methods
The CVD diamond films were grown on a silicon (001) substrate by using a microwave plasma-assisted CVD stainless steel reactor. A microwave power of 1400W and a substrate temperature of 800°C were used. The CVD films were grown during 15 hours by using 9% of CH4 and 1.25% of CO2 gas mixture, followed by 15 hours of growing with the same mixture composition and adding 750 ppm of nitrogen to the precursor gas. Finally, two kinds of diamond films were obtained, a nominally undoped sample (U1), containing around 10 ppm of N2 due to atmospheric and precursor gas component contamination and the doped sample (H750) contain 750 ppm of N2 which was incorporated into the precursor gas used. The 60Co gamma irradiations were performed by using a Gammabeam 651PT Nordion irradiator with an 81.11 Gy/min dose rate. The TL measurements were carried out in a Harshaw TLD 3500 system employing a heating rate of 5 °C s⁻¹, in a nitrogen atmosphere to avoid spurious TL signals. Previously to irradiation, samples were heated at 400°C for 2 minutes and TL readouts were performed 2 minutes after gamma irradiation.

The micrographs were obtained with a Scanning Electron Microscopy (SEM) JEOL/JSM model 5900-LV equipped with an (EDS) Oxford ISIS (Si–Li) detector having an energy resolution of 133 eV at 5.9 keV and detector area of 10 mm².

3. Results and discussion

3.1. Characterization of the samples
Figure 1 shows the scanning electron micrograph (SEM) of U1 (a) and H750 (b) diamond film surfaces. Polycrystalline morphology of microcrystallites ranging from 1 to 10 μm and without specific shape and without preference orientation can be observed in the micrograph (a). In (b), the particle morphology of 750 ppm hydrogen doped CVD diamond powder is almost spherical and the size of particles obtained was ranging from 1 to 5 μm. It seems that the presence of high nitrogen concentration during the preparation sample may help to obtain good nucleation centers on the substrate forming a homogeneous spherical particle and improving the polycrystalline morphology of the diamond. The energy dispersive spectroscopy (EDS) analysis shows carbon and oxygen ions in both samples. In the second one, the presence of silicon may be due to the migration ions from the surface of the substrate. Also, traces of sodium presence was detected, and it may come from the possible contamination of the silicon substrate. Several authors have been observed different ions contaminants in diamond samples that come from mainly to the mixture of gases and experimental conditions of the synthesis [11-13].

3.2. Thermoluminescence dose response
Figure 2(a) shows the dose-response (defined as the integrated area under the glow curve) as a function of the dose of both samples. In order to compare the TL intensity of H750 sample was multiplied by 100. For both samples, the TL response was evaluated in the dose range between 100 Gy and 10 kGy.

As can be seen from figure 2(a), TL intensity of sample U1 is two orders of magnitude higher than sample H750 for doses between 100 and 500 Gy. On the other hand, for higher doses than 700 Gy, the TL intensity of the U1 sample reaches a saturation stage whereas that H750 sample keeps increasing as a function of the dose.

The behavior of the TL glow curves of U1 and H750 can be observed in figures 2(b) and 2(c), respectively. It is possible to see that after the fourth curve, the glow curve reaches a saturation stage. On the other hand, it is evident from figure 2(c) that for doses higher than 700 Gy (fifth curve), the second glow peak centered at 140°C starts to grow with greater intensity.
Figure 1. Scanning electron micrograph and energy dispersive spectroscopy of U1 (a) and H750 (b).

Figure 2. In (a), TL response of U1 (solid circle) and H750 (open square) samples from 90 Gy up to 10 kGy. In (b) and (c) are the glow curves of sample U1 and H750 at the same doses, respectively.

3.3. TL dosimetric properties for high-dose gamma irradiation for H750 sample
To evaluate the feasibility of using the H750 sample as a high-dose TL detector, the TL dose-response, the repeatability of the TL signal, and the fading in the nitrogen-doped samples were analyzed.
It was studied the dose range ranging from 700 Gy up to 10 kGy because the interest to obtain a diamond radiation detector for high doses.

In figure 3 a good linearity in the interval ranging from 700 Gy up to 10 kGy is observed. It was found better linearity if it is used the height of the second glow peak (Adj. R²=0.990) in place of the area under the glow curve (Adj. R²=0.979) for determinate the absorbed dose.

Besides, the repeatability of the TL response was studied. The sample was irradiated with a 2.5 kGy gamma dose. After 17 consecutive cycles of irradiation, heating and readout, a good reproducibility was obtained with a percentage standard deviation lower than 2.5%.

Finally, a fading study was carried out. The sample was irradiated with 2.5 kGy and stored in darkness and at room temperature during different periods. The TL signal decreased up to 60% in the first 24 hours and then, the signal remains constant. It can be due to the presence of shallow traps presents in the sample.

3.4. Glow curve deconvolution

To determine the kinetic parameters of the TL glow peaks, a glow curve deconvolution was carried out by assuming a General Order Kinetic (GOK) model modified by Rasheedy [14]. This model includes the ratio n₀/N which takes into account the fraction of occupied traps. The effectiveness of fit was evaluated using the figure of merit (FOM) [15]. A FOM equal or less than 5% means a very good fitting. Figure 4 shows the deconvolution of the TL glow curve recorded to 10 kGy, 5 kGy, and 700 Gy, from top to bottom, respectively. In all cases, glow curves were deconvolved in four TL glow peaks. The activation energy values (E = 0.84, 0.74, 0.82, and 1.05 eV), and the first and second-order kinetics (b = 1.7, 2.0, 2.0, 1.0) were determined for the first to fourth peaks, respectively, obtained with 700 Gy. Similar kinetics parameter values were obtained for the other high doses. It was observed that the last peak reaches the saturation because the deepest trap is almost full, namely, n₀/N near to 1. On the other hand, the second one keeps growing with dose, i.e., 1.8×10⁻³, 5.0×10⁻³, and 7.2×10⁻³ for 0.7, 5, and 10 kGy, respectively.

In order to investigate the kinetic parameters after different preheat temperatures, in figure 5 it is possible to see the deconvolution of the TL glow curve of the sample irradiated with a dose of 2.5 kGy and heated at 100, 200, and 250°C for 10 seconds, respectively.
Table 1 shows the kinetic parameters obtained for sample H750 irradiated with 2.5 kGy, and heated at 100, 200, and 250°C, respectively. In the case of the sample heated at 200°C the first and second glow peaks disappear completely, and for 250°C the same occurs for the third one. The kinetic parameters values obtained are close to those for the glow curves at different doses (Fig.4). The advantage to use the preheat temperature at 200°C allows erase the low peaks of the glow curves and to obtain a dosimetric glow peak that may be useful for dosimetry purposes and the fading can be improved.

**Figure 4.** Glow curve deconvolution (solid gray line) of the TL glow curves (solid circles) of sample H750 recorded to 10000, 5000, and 700 Gy (from top to bottom), respectively.

**Figure 5.** Deconvolution (solid gray line) of the TL glow curves (solid circles) of sample H750 irradiated with a dose of 2.5 kGy and heated at 100, 200, and 250°C, respectively.

| Heated at | Peaks | $E$ [eV] | $s$[s$^{-1}$] | $b$ | $n_0/N$ | FOM |
|-----------|-------|----------|--------------|-----|----------|-----|
| 100°C     | Peak #1 | 0.81     | 3.0\times10^{12} | 1.8 | 5.2\times10^{-4} |     |
|           | Peak #2 | 0.76     | 2.6\times10^{11} | 2.1 | 1.7\times10^{-3} | 1.1%|
|           | Peak #3 | 0.84     | 3.5\times10^{10} | 2.0 | 2.4\times10^{-3} |     |
|           | Peak #4 | 1.05     | 2.4\times10^{9}  | 1.1 | 0.83     |     |
| 200°C     | Peak #1 | -        | -             | -   | -        |     |
|           | Peak #2 | -        | -             | -   | -        |     |
|           | Peak #3 | 0.84     | 3.6\times10^{10} | 2.0 | 2.18\times10^{-3} | 1.5%|
|           | Peak #4 | 1.05     | 2.4\times10^{9}  | 1.1 | 0.83     |     |
| 250°C     | Peak #1 | -        | -             | -   | -        |     |
|           | Peak #2 | -        | -             | -   | -        |     |
|           | Peak #3 | -        | -             | -   | -        |     |
|           | Peak #4 | 1.07     | 4.2\times10^{9}  | 1.3 | 0.07     |     |
4. Conclusion
In this work, TL dosimetric properties of high-dose gamma-irradiated CVD diamond films were investigated. Samples of nitrogen-doped CVD diamonds showed good linearity in the dose range from 700 up to 10000 Gy which is a very good advantage against other CVD diamonds that present a saturation for doses higher than 500 Gy. This dose range is optimal for high dose dosimetry.

Besides, good repeatability of the TL response with a percentage standard deviation lower than 2.5% has been found and the fading study showed that the TL glow curve decreases up to 60 % in the first 24 hours and then the signal remains constant. These TL dosimetric properties make the nitrogen-doped CVD diamond a promising material to be used in gamma-radiation dosimetry.

Finally, to analyze the kinetics parameters associated with the trap distribution in the CVD diamond, a computerized deconvolution was carried out by using the general order kinetics (GOK) model, and the similar kinetic parameter values were obtained for three different irradiation doses and three different heating temperatures. The activation energy values were between 0.76 and 1.05 eV and the frequency factor values between 109 and 1012 s-1. For all cases, acceptable FOMs lower than 2% were obtained.

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References
[1] Attix F, Roesch W C and Tochilin E 1968 *Radiation Dosimetry* vol 1 (New York: Academic Press) chapter 4
[2] Ramkumar S, Buttar C M, Conway J, Whitehead A J, Sussman R S, Hill G and Walker S 2001 *Nucl. Instr. and Meth. A* **460** 401
[3] Benabdesselam M, Nakamura S M, Serrano B, Iacono P, Wrobel F, Lapraz D, Herault J and Butler J E 2006 *Radiat. Prot. Dosim.* **120** (1–4) 87
[4] Borchi E, Furetta C, Kitis G, Leroy C, Sussman R S and Whitehead A J 1996 *Radiat. Prot. Dosim.* **65** 291
[5] Marczewska B, Bilski P, Desladek M, Olko P, Rebisz M and Waligorski M P R 2002 *Radiat. Prot. Dosim.* **101** (1–4) 485
[6] Marczewska B, Thompson D, Descamps C, Bilski P, Schirru F, Nowak T and Bogus A 2007 *Phys. Status Solidi A* **204** (9) 3036
[7] Schirru F, Marczewska B, Tallaire A, Achard J, Nowak T and Olko P 2007 *Phys. Status Solidi A* **204** (9) 3030
[8] Gastélum S, Cruz-Zaragoza E, Favalli A, Chernov V, Meléndrez R, Soto-Puebla D, Pedroza Monerton M and Barboza-Flores M 2007 *Phys. Stat. Sol. (a)* **204** (9)
[9] Gastélum S, Cruz-Zaragoza E, Favalli A, Meléndrez R, Chernov V and Barboza-Flores M 2008 *Diamond & Rel. Mater.* **17** 1283
[10] Biggeri U, Borchi E, Bruzzi M, Leroy C, Sciortino S, Bacci T, Ulivi L, Zoppi M and Furetta C 1996 *Il Nuovo Cimento* **109A** (9) 1277
[11] Gracio J J, Fan Q H and Madaleno J C 2010 *J. Phys. D: Appl. Phys.* **43** 374017
[12] Mitura Nowak M, Karczmarska A, Marczewska B and Marszalek M 2013 *Phys. Status Solidi A* **210** (10) 2083
[13] Zaitsev A M, Moe K S and Wang W 2017 *Diamond & Related Materials* **71** 38
[14] Rasheddy M S 1993 *J. Phys.: Condens. Matter* **5** 633
[15] Horowitz Y S and Yossian D, 1995 *Radiat. Prot. Dosim.* **60** 1