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# Characterization of B-doped polycrystalline diamond films using thermally stimulated luminescence

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## Abstract

The effect of different rates of boron incorporation during the growth in diamond on the thermoluminescence (TL) features of this material is investigated. TL studies performed between liquid nitrogen temperature (LNT) and 320 K show some phosphorescence and two other peaks at 226 and 266 K. For the first time, boron level in polycrystalline diamond films was identified by TL by an intense glow peak at 226 K and activation energy of about 0.35 eV. For this main peak, spectral analysis shows a prominent broad band luminescence peaking at 2.56 eV. At 77 K, another emission band was observed at 2.22 eV. This is in agreement with the fact that the recombination mechanisms involve two different recombination centers and, therefore, phosphorescence at 77 K and the main peak at 226 K are of different nature, i.e. the TL peak at 226 K is due to boron while phosphorescence is hence, probably due to a shallow donor level. The behavior of TL intensity relative to the main component at 226 K observed on all the films and linked to boron level decreases with increasing boron concentration.

*Keywords:* Thermoluminescence, CVD diamond, Boron, Impurity incorporation

## 1. Introduction

Boron doped polycrystalline diamond films grown by Chemical Vapor Deposition (CVD) have a wide array of potential applications like high temperature electronics and electrochemistry. Thermoluminescence of semiconducting diamond has been reported by many authors [1-2]. Recently, a large amount of work has been carried out by Keddy et al. [3-4] on synthetic crystals. They particularly reported that the incorporation of about  $2 \times 10^{17} \text{ cm}^{-3}$  of boron in these crystals leads to an increase of both the sensitivity and the linearity of the TL response by comparison with undoped crystals. In the case of boron doped polycrystalline films, we already reported the TL properties but specifically after excitation at room temperature (RT) [5]. To our knowledge, there is only one other paper dealing with TL studies on this material, also from RT and without any indication on TL behavior of boron itself [6]. The purpose of the present study is to characterize more precisely this most prominent impurity in diamond and to determine the effect of its incorporation on TL properties of CVD diamond. It reveals a green-emitting glow peak in addition to the blue one observed previously in natural stones [1]. The green emission relative to phosphorescence at 77 K, has to our knowledge, not yet been reported. The energy level as well as the other trapping parameters (kinetics recombination, frequency factor ...) and luminescence features relative to boron in polycrystalline diamond are reported here by TL.

## 2. Experimental conditions

Three polycrystalline diamond films have been studied by thermoluminescence. They were grown by the Microwave Plasma CVD (MWCVD) technique at the Naval Research Laboratory. They were deposited on tungsten substrate with a growth rate of  $1 \mu\text{m/h}$ . Synthesis conditions and characteristics of the films are summarised in table 1. Boron doping was achieved by adding 0.1% diborane ( $\text{B}_2\text{H}_6$ ) diluted in hydrogen, to the gas phase. This led to [B] rates of 3.3, 6.2 and 9.7 ppm in films NRL140, NRL143 and NRL144 respectively. The film color moves from light blue (NRL140) to dark blue (NRL144) with increasing boron rate and all these heavily B-doped films were of the same size ( $5 \times 5 \text{ mm}^2$  squares).

For TL measurements, the films were irradiated in vacuum at LNT by a Deuterium (DUV) lamp (200-400 nm, 50 W) without filtration.

Two minutes after excitation, TL readout was achieved by linear heating of the film from LNT to 320 K at a rate of 0.5 K/s. Luminescence intensity versus increasing temperature was recorded by means of a photomultiplier (250-600 nm). For spectral analysis of TL, emission spectra were detected by an optical multi-channel analyzer working between 300 and 800 nm.

### 3. Results and discussion

Fig. 1 shows normalized TL curves relative to 3 polycrystalline diamond films. The glow curve of the lightly doped film (NRL140) is more than 4 times intense than the two others and is characterized by high phosphorescence. This phosphorescence means that one (or more) traps level occurs at near to 77 K. In addition, one can see a main peak at 226 K accompanied by a shoulder at 266 K. The glow curve relative to the moderately boron doped film (NRL143) shows also some phosphorescence as well as the main component at 226 K while the shoulder at 266 K is tightly reduced. In the case of the heavily doped film (NRL144), the shoulder at 266 K is disappeared but even reduced, the main TL component at 226 K as well as the phosphorescence still remain. Increasing of boron concentration in the films leads to the decrease of their TL response. Glow curves show that increasing in boron doping led to the concentration reduction of the defects relative to both phosphorescence and the peak at 266 K. We focus our attention on the analysis of the TL curve of the film NRL140 between 160 and 320 K. In this range, it consists of the main peak at around 226 K and the shoulder at 266 K. Spectral analysis based on the 3D TL measurements discussed later showed that for these two neighboring components, TL emission mechanism consists of two traps and one common recombination centre. If one assumes that the two traps do not interact with each other and the constituent peaks are independent, thus a mere superposition of the constituent peaks yields to the observed TL glow curve. The rate equations for superposition of the two peaks independent of each other are [7]:

$$\frac{dn_i}{dT} = -\frac{f_i}{q} n_i \exp\left(-\frac{E_i}{kT}\right) + \frac{\beta_i(N_i - n_i)n_{ci}}{q} \quad (1)$$

Where  $i = 1$  and  $2$ ,  $n_i$  is the density of electrons in  $i$ -th trap of which the trap depth is  $E_i$ ,  $n_{ci}$  is the trap density in the conduction band.  $N_i$  is the density of  $i$ -th trap,  $f_i$  is its frequency factor,  $\beta_i$  is the probability for a released carrier to be captured by the  $i$ -th trap. In addition,  $q$  is the heating rate,  $k$  the Boltzmann's constant and  $T$ , the absolute temperature

$$\frac{dn_{ci}}{dT} = -\frac{dn_i}{dT} - \frac{\gamma_i n_{ci} h_i}{q} \quad (2)$$

$$\frac{dh_i}{dT} = -\frac{\gamma_i n_{ci} h_i}{q} \quad (3)$$

Where  $\gamma_i$  indicates the recombination probability and  $h_i$  is the density of recombination centers. Equations above satisfy the condition of charge neutrality at any temperature and where the density of thermally disconnected deep traps is taken into account:

The observed TL intensity is expressed as:

$$I_{TL} = \sum_{i=1}^2 C_i \gamma_i h_i n_{ci} \quad (4)$$

$C_i$  is a geometrical constant of the apparatus including the luminescence efficiency of the material.

Results of curve fitting are shown on Fig. 2, the standard deviation  $\delta^2$  value between experimental data and the theoretical ones is  $4.2 \times 10^{-3}$  and the trapping parameters are shown in Table 2.

Simulations results led to  $C_2 = 1.02 C_1$  meaning that the luminescence efficiencies accord with each other. This refers to the same kind of recombination centre in both peaks at 226 K and 266 K. In fact the recombination probabilities  $\gamma_1$  and  $\gamma_2$  were respectively  $4.9 \times 10^{-16}$  and  $4.8 \times 10^{-16} \text{ s}^{-1} \text{ cm}^{-3}$  when a value of  $10^{15} \text{ cm}^{-3}$  was used as the initial value for trap density,  $N_1 + N_2$ . Activation energies relative to these peaks are  $0.35 \pm 0.03 \text{ eV}$  and  $0.44 \pm 0.04 \text{ eV}$  respectively.

Curve fitting analysis, based on the same equations governing the TL process applied to the main peak at 226 K observed on the glow of the NRL143 film reveals an energy depth of  $0.34 \pm 0.03 \text{ eV}$ . This energy level is in agreement with the value obtained on the main peak presented by the NRL140 film.

The activation energy of this acceptor level is in very good agreement with the value obtained on boron-doped CVD diamond by deep level transient spectroscopy (DLTS) method [8]. This main TL component having activation energy of  $\sim 0.35 \text{ eV}$  is therefore, according to the literature, assigned to thermal release of holes from the boron level. Boron atoms located at substitutional sites in the diamond film induce electrically active defects and introduce an acceptor level with activation energy at about  $0.36 \text{ eV}$  into the band gap of the diamond film.

Variations of normalized TL intensity of this main peak as a function of boron amount in the films match perfectly an exponential decay whose equation allows us to predict that for polycrystalline films with boron content higher than 11 ppm, no TL signal can be detected. This fact is due to the increase with boron concentration of the optical absorption factor in visible. The value of 11 ppm is in quite good agreement with the optimal one that we suggested earlier as less than 15 ppm [5].

Concerning the peak at 266 K whose corresponding trap depth is around  $0.44 \text{ eV}$  has, to our knowledge, never been reported in the literature.

Phosphorescence observed at 77 K on the three films is due to one shallow level whose thermal ionization occurs at temperatures nearby 77 K but that we cannot characterize due to the limitation of the equipment below 77 K.

Afterwards, spectral analysis of TL was carried out on the films. On Fig. 3, one can see two different features at 77 and (226/266 K): the distribution obtained during phosphorescence is characterized by a broad band centered at 2.22 eV and a more intense one located at 2.56 eV, common to peaks at 226 and 266 K, meaning that both peaks are linked to the same recombination centre.

These new features let us assume that the trap levels relative to 77 K phosphorescence on the one hand and to TL peaks at (226/266 K) on the other hand are of different nature. Since the peak at 226 K is relative to boron known as corresponding to an acceptor level, one can conclude that the neighbor traps with an energy level of 0.44 eV relative to the peak at 266 K have also an acceptor character whereas the 77 K phosphorescence corresponds to a shallow donor trap level. This last statement is in agreement with the literature where a TL peak observed at 50 K on synthetic stones, was attributed to a donor level located at 0.02 eV below the conduction band [9].

The tentative model proposed to explain the TL process involved in the films is schematically represented by the energy band diagram in Fig. 4.

#### **4. Conclusion**

The studied films show phosphorescence at 77 K and one main peak at 226 K. The activation energy of this main peak is 0.35 eV and is linked to boron acceptor level. The different nature of the two emissions let us to suppose that this phosphorescence (emission at 2.22 eV) might be due to a shallow donor level while both peaks at 226 and 266 K (emission at 2.56 eV) correspond to thermal release of holes from the acceptor levels at 0.35 and 0.44 eV. To explain the TL process occurring in the film during heating, a schematic model for the thermally activated transitions of carriers is presented.

Boron doping leads to a decrease of TL response. This decrease is attributed to enhancement of the optical absorption factor in visible and consequently to marked loss of TL intensity.

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## FIGURE CAPTIONS

FIG. 1: Thermoluminescence glow curves obtained on the different polycrystalline films after 10 min. of DUV illumination at 77 K.

FIG. 2: Computerized deconvolution of the NRL140 TL curve obtained after 10 min. of DUV illumination at 77 K.

FIG. 3: Spectral analysis of the phosphorescence (a) and glow peaks at 226 and 266 K (b) recorded after 10 min. of DUV illumination at 77 K.

FIG. 4: Schematic model for the transitions involved in the excitation of the two emissions bands observed on film NRL140. The broken line corresponds to the mid-gap (2.75 eV) of diamond

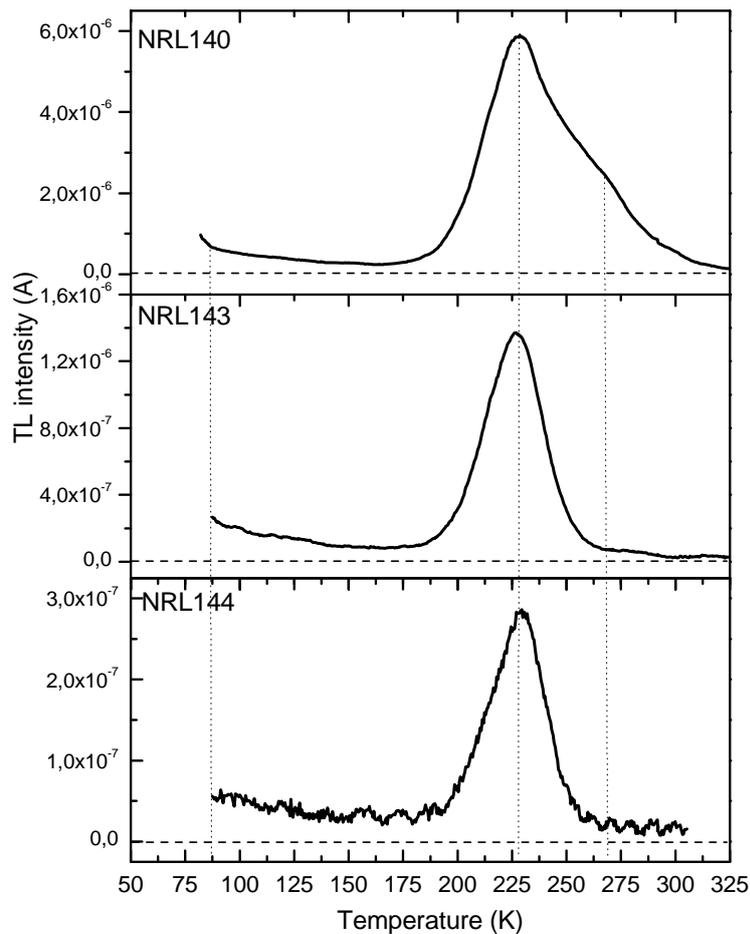


Fig. 1

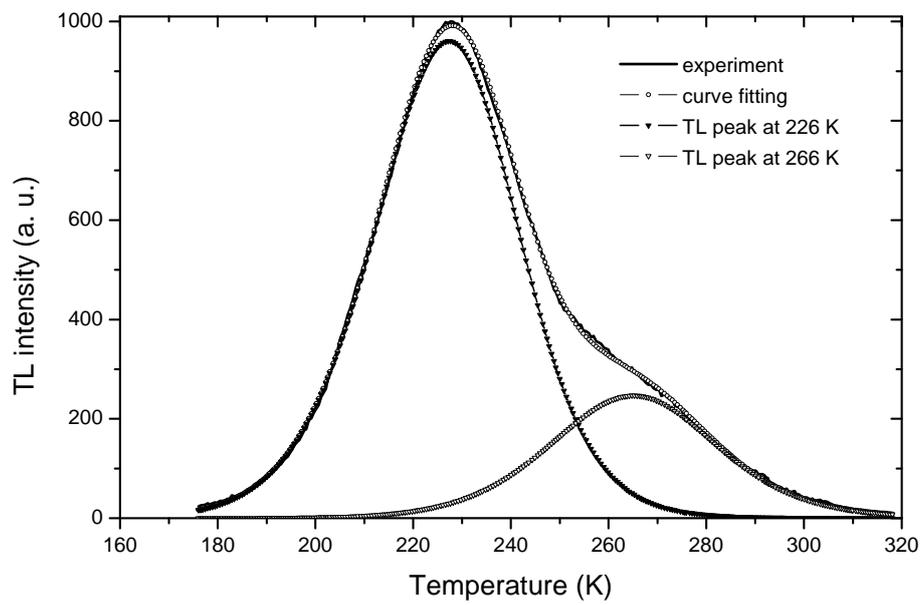


Fig. 2

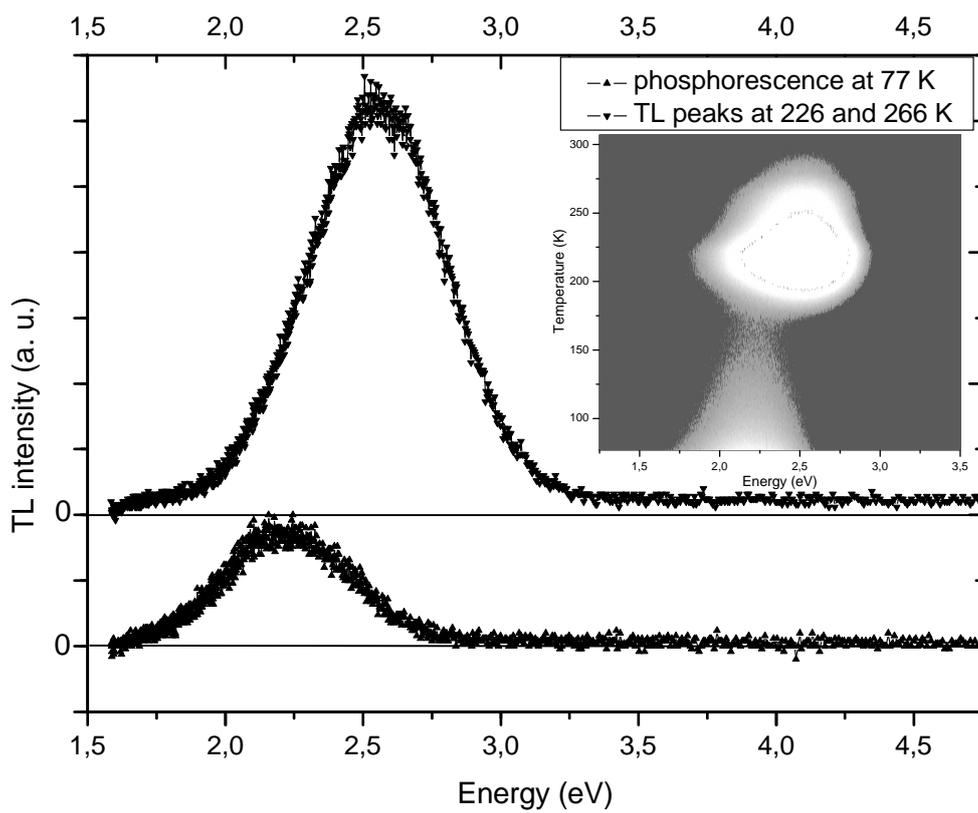


Fig. 3

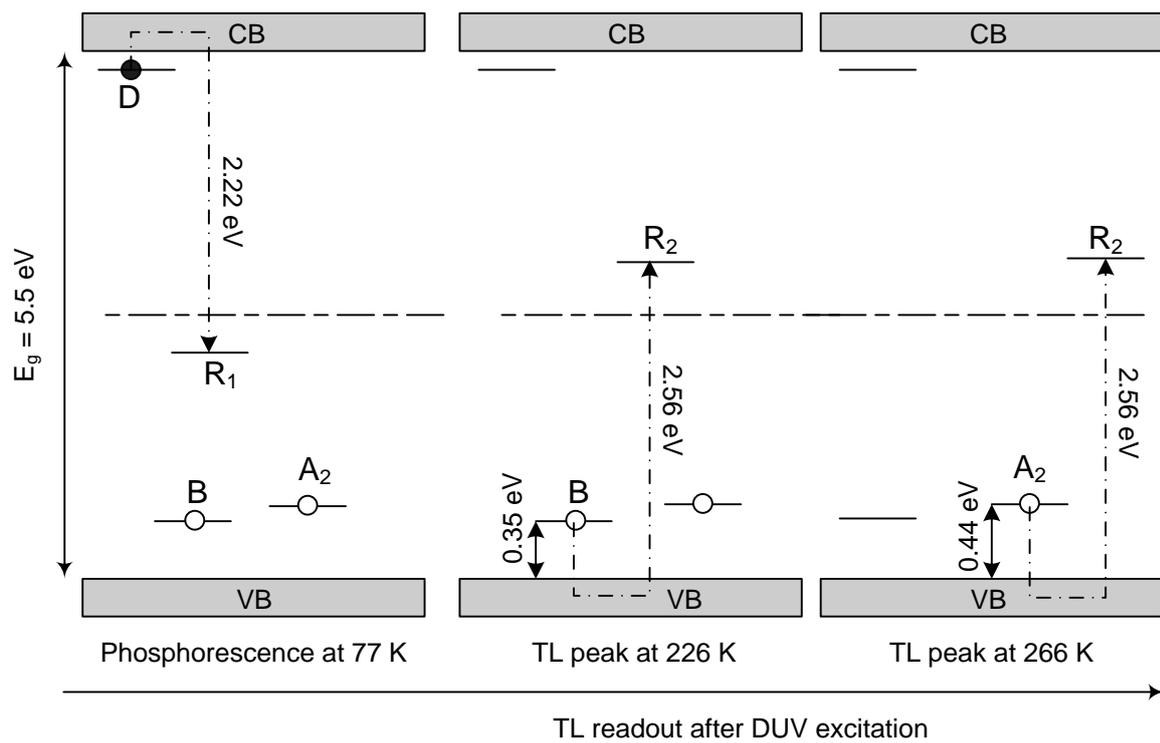


Fig. 4