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Mourad Benabdesselam, A. Petitfils, Frédéric Wrobel, J. E. Butler, Franck Mady. Thermal quenching investigation in CVD diamond by simultaneous detection of thermally stimulated luminescence and conductivity.. *Journal of Applied Physics*, 2008, 103, pp.114908. 10.1063/1.2937243 . hal-00530726

HAL Id: hal-00530726

<https://hal.science/hal-00530726>

Submitted on 29 Oct 2010

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Thermal quenching investigation in CVD diamond by simultaneous detection of thermally stimulated luminescence and conductivity.

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Chemical Vapor Deposited (CVD) diamond is a very promising material extensively studied in many technologies. Thermoluminescence (TSL) experiments demonstrate that important thermal quenching phenomenon occurs with microwave plasma chemical vapour deposited (MWCVD) diamond. This phenomenon leads to a large discrepancy on the determination of electronic trap parameters. Thermally stimulated conductivity phenomenon is not affected by thermal quenching and allows an easier determination of trap parameters than TSL measurements. The difference between the both ways of trap energy computation is found to be around 4% instead of 28% obtained when thermal quenching is failed.

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I. INTRODUCTION

In the field of dosimetry and microelectronics, the activation energy of a trap in the band gap of an insulating material is one of the most important parameters characterising the relative point defect in this material. Nevertheless, the determination of this parameter may lead to many discrepancies sometimes obscuring everything in the physical sense when sufficient precautions are not taken. In the case of luminescent materials, thermally stimulated luminescence (TSL) and/or thermally stimulated conductivity (TSC) peaks are characteristic of the trap level involved in the luminescence of these materials. From TSL glow curves, several methods based on the shape of the peak¹ and experimental ones like the use of various heating rates² or the extensively used “initial rise” technique are used to determine the trap parameters. This last method is based on the observation from Garlick et al.³ that the initial part of the TSL curve is exponentially dependent on temperature. For the TSC process, the theory of Haering et al.,⁴ based on several measurements using different heating rates, allows determination of the trap depth in the material. This work details the decrease of luminescence efficiency as the temperature increases, commonly known as thermal quenching phenomenon, which on one hand, does not affect the TSC where no recombination mechanism of charges is involved, but which can have, on the other hand, a detrimental effect on TSL features of a material when it exists. In this paper, the activation energy of the main trap involved in CVD diamond is determined by both TSC and “Initial Rise” TSL measurements. The evidence of the presence of thermal quenching phenomenon in the main thermoluminescent peak of diamond allows the correction of the parameters obtained by TSL analysis, and thus a comparison with the TSC results is obtained.

II. MATERIALS AND EXPERIMENTAL DETAILS

Measurements were carried out on a set of 21 unintentionally doped free standing polycrystalline diamonds films synthesized at the Naval Research Laboratory (NRL) by microwave plasma-assisted CVD. Growth was realized on a tungsten substrate heated at 1023 K with a microwave power of 4.5 kW and a gas pressure of 15.4 kPa. Flow rates of hydrogen and methane were 156 and 6.3 sccm respectively. The studied films are squares of dimensions (5×5) mm² and 260 μ m thick.

A. TSL measurements

Prior to heating, the films were irradiated at room temperature (RT) by X rays (Cu target, 45 kV, 2 m). The air kerma rate was 13.48 Gy x min⁻¹.

TSL glow peaks were detected by a Philips XP-2262B photomultiplier (PM) tube (300-600 nm spectral range). After irradiations, the diamond was depleted of trapped charge carriers in shallow traps by preheating up to 483 K and then TSL readout was performed from RT to 673 K with a linear heating rate of 1 K/s. In order to see the effect of the heating rate on the TSL response, a set of measurements with various heating rates ranging from 0.17 K/s to 10 K/s were conducted.

B. Simultaneous TSL/TSC detection

After irradiations, simultaneous TSL and TSC measurements were achieved at RT under vacuum (10^{-5} Torr) by means of another experimental setup. Half of the sample surface is covered by silver contact for TSC measurements and thus to detect sufficient TSL emission a high dose is delivered (5 minutes, 45 kV, 10 mA corresponding to an air kerma rate of 30.29 Gy x min⁻¹). The sample is heated from 273 K to 673 K at a heating rate of 1 K/s. Electrons are collected via copper electrode linked to a Keithley (model 617) electrometer. Applied electric field is 2.3×10^3 V/cm (breakdown voltage at $\sim 10^7$ V/cm).

III. RESULTS

A. TSL measurements – luminescence efficiency – activation energy determination

The luminescence efficiency of a material is described as the ratio of the radiative recombination probability (P_r) to the total recombination (P_r+P_{nr}) where P_{nr} is the probability of non-radiative recombinations.

$$\eta(T) = \frac{P_r}{P_r + P_{nr}} \quad (1)$$

The radiative probability P_r is not affected by temperature, while the non-radiative probability increases with temperature. For this reason, numerous TSL measurement were carried out at different heating rates varying from 0.5 to 10 K/s. Whatever is the irradiation mode (UV or X-rays), the normalized area of the main TSL peak is plotted as a function of heating rate (Fig. 1). This figure points out that strong luminescence decay occurs in these CVD diamond films (loss of almost 50% on the dose information stored in the TSL peak in one decade of heating rate). The spectral emission of this main peak is the so-called A-band luminescence peaking at 2.55 eV.⁵

The origin of this phenomenon has been tested using Mott and Seitz theory.⁶⁻⁷ This theory stipulates that an excited state can decay to the ground state via radiative or non-radiative transitions.⁸⁻⁹ In the configurational diagram shown in Figure 2, the electron is in an excited state of a recombination centre at the minimum of energy (B). Direct transition from B to C is a radiative transition and then the electron can decay from C to A via phonon emission. By absorbing an external thermal energy input (W), the electron in B rises to a higher excited state D. From this higher state the electron can transfer to the ground state by a variety of processes without emission of radiation. This transition is then non-radiative and the luminescence efficiency is expressed as:

$$\eta(T) = \frac{1}{1 + c \exp\left(-\frac{W}{kT}\right)} \quad (2)$$

where c is a dimensionless factor and W , the thermal activation energy (eV) of non-radiative transitions. The non-radiative probability P_{nr} depends on temperature through the Boltzmann factor. Fitting the parameters c and W to experimental curves obtained for CVD diamond leads to the values of 7.07×10^4 and 0.49 eV respectively. Figure 3 displays the plot of the luminescence efficiency according to (2) with the values of c and W parameters determined above. A very good agreement between the theoretical plot and the experimental results is observed. The typical glow curve and the TSL peak area values for different heating rates not corrected from thermal quenching are also shown. To highlight the detrimental effect of thermal quenching in CVD diamond, we show in Figure 4 the experimental TSL curve which detects only the radiative emission and the theoretical one considering the additional non-radiative transitions. Both curves are obtained with a same heating rate of $q = 1 \text{ K/s}$. This figure demonstrates that the trap defect signature (activation energy E or escape frequency s) using the experimental initial rise method¹⁰ might be erroneous and thus corrections need to be applied. For this, the corrections have been developed in the literature.¹¹⁻¹² The trap parameters determined experimentally by initial rise method without considering thermal quenching are $E = (0.88 \pm 0.04) \text{ eV}$ and $s = 2.6 \times 10^6 \text{ s}^{-1}$. After correction a new set of parameters is obtained, $E = (1.22 \pm 0.06) \text{ eV}$ and $s = 2.9 \times 10^9 \text{ s}^{-1}$. The processes used to determine the thermal quenching features and the trapping parameters are detailed in a previous paper.¹³

B. Simultaneous TSL/TSC measurement – Trap activation energy determination

The TSL and TSC curves obtained simultaneously are shown on Figure 5. Both curves are characterized by a same component peaking at different temperatures. Indeed, the TSL

peak is located at 524 K whereas TSC one occurs at slightly higher temperature (533 K). This temperature shift is commonly observed between the two phenomena.¹⁴⁻¹⁵ On the basis of a simple model, the intensity of the TSL signal I_{TSL} depends on both the concentration of electrons released in the conduction band (CB) and that of trapped holes in the recombination centre:

$$I_{TSL}(T) \propto \gamma \times n_c(T) \times n_h(T) \quad (3)$$

where n_c and n_h designate the density of free electrons in the CB and that of trapped holes, γ is the recombination coefficient. In the case of TSC process, the intensity depends only on the density of free electrons in the CB:

$$I_{TSC}(T) = A \times n_c(T) \quad (4)$$

where A is a proportionality factor depending on the applied electric field, the electron mobility μ , the electric charge e and the experimental TSC device.

According to (3) and (4), the temperature shift observed between the two curves shown on Figure 5, might be attributed to the fact that the hole concentration which plays a role only in the TSL intensity decreases with increasing temperature.

The determination of the trap activation energy is based on the theory of Haering et al.⁴ and applied to the TSC curve. The geometrical factor μ_g defined by Halperin et al.¹⁶ is determined from the curves by taking (or not) into account the thermal quenching. The obtained values of μ_g are 0.44 and 0.46 respectively. These values of the shape factor correspond to a first order kinetics.¹⁷ The first order kinetics is characterised by a sharp peak with a rapid decay of the TSL intensity above the peak maximum, as one can see in Figures 3, 4 and 5. According to this observation, the Haering theory is applied in the case of weak retrapping:

$$(N - n_c) \times \sigma_e \times \nu \ll \tau^{-1} \text{ with } N \text{ the concentration of traps, } n_c \text{ the density of conduction}$$

electrons, σ_e the capture cross section of electrons, ν the electron thermal velocity in the CB and τ is the mean recombination lifetime of electrons.

The electrical conductivity is therefore: ⁴

$$\Sigma(T) = N_c \sigma_e \nu \times \mu \tau \times e n_0 \times \exp\left(-\frac{E}{kT} - \frac{1}{q} \int_{T_0}^T N_c \sigma_e \nu \exp\left(-\frac{E}{kT}\right) dT\right) \quad (5)$$

with n_0 the concentration of electrons in traps, q the heating rate, k the Boltzmann's constant, T the absolute temperature (K), E the trap activation energy (eV) and N_c defines the effective density of states in the conduction band and T_0 the initial temperature.

By differentiating $\ln[\Sigma(T)]$, we obtain:

$$\exp\left(\frac{E}{kT_m}\right) = \frac{N_c \sigma_e \nu}{q} \times \frac{kT_m^2}{E} \quad (6)$$

T_m corresponds to the temperature at which the conductivity is at its maximum.

Then by the use of two different heating rates q_1 and q_2 the theory of Hearing leads to the activation energy of the trap since N_c , σ_e , and ν do not depend on the heating rate:

$$E = \ln\left[\left(\frac{T_{m1}}{T_{m2}}\right)^2 \times \frac{q_2}{q_1}\right] \times \frac{k \times T_{m1} \times T_{m2}}{T_{m2} - T_{m1}} \quad (7)$$

By applying this measurement protocol to the diamond film studied with heating rates of 0.17 K/s and 1 K/s, we obtain a trap depth $E = (1.18 \pm 0.04)$ eV.

This value obtained by TSC is in a very good agreement (deviation of 4%) with that determined by TSL when taking into account the thermal quenching.

IV. CONCLUSION

Thermal quenching is an important phenomenon in CVD diamond. If trap parameters are determined using the initial rise method of TSL analysis, the luminescence decay leads to an underestimation of these parameters. Indeed, a deviation of almost 30% is observed between activation energy values determined experimentally with and without correction of the curves from thermal quenching. The TSC measurement is not affected from thermal quenching since no recombination process is involved in this phenomenon. According to Haering's theory for TSC, two measurements at two different heating rates led to an activation energy value in excellent agreement with that obtained in TSL by the initial rise method but corrected from thermal quenching. However, the TSL technique is a very interesting tool of investigation of materials and their characterisation and is still very convenient particularly in the field of ionising radiation Dosimetry. But for more accurate analysis of point defects (intrinsic or impurities) occurring in a material, the TSC method is more practical since it requires a very few number of measurements and the disadvantage of thermal quenching is avoided.

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FIGURE CAPTIONS

FIG. 1: Normalized TSL peak area as a function of various heating rates in MWCVD diamond after X-rays irradiations at RT.

FIG. 2: Configurational coordinate diagram according to Mott-Seitz quenching mechanism

FIG. 3: Luminescence efficiency, TSL curve and normalized TSL signal for different heating rates, presented as full gray stars.

FIG. 4: Experimental TSL curve (solid line) and contribution of the non-radiative transitions (dashed line).

FIG. 5: TSL and TSC curves obtained simultaneously on a MWCVD diamond with a heating rate of 0.5 K/s after X-rays irradiations at RT.

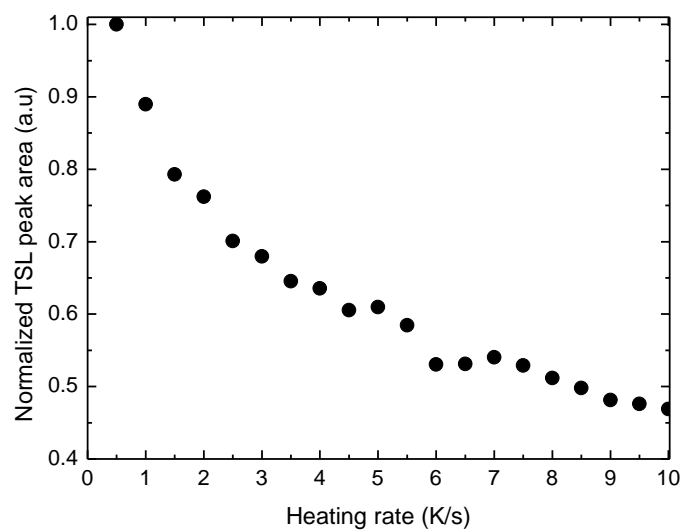


Fig 1

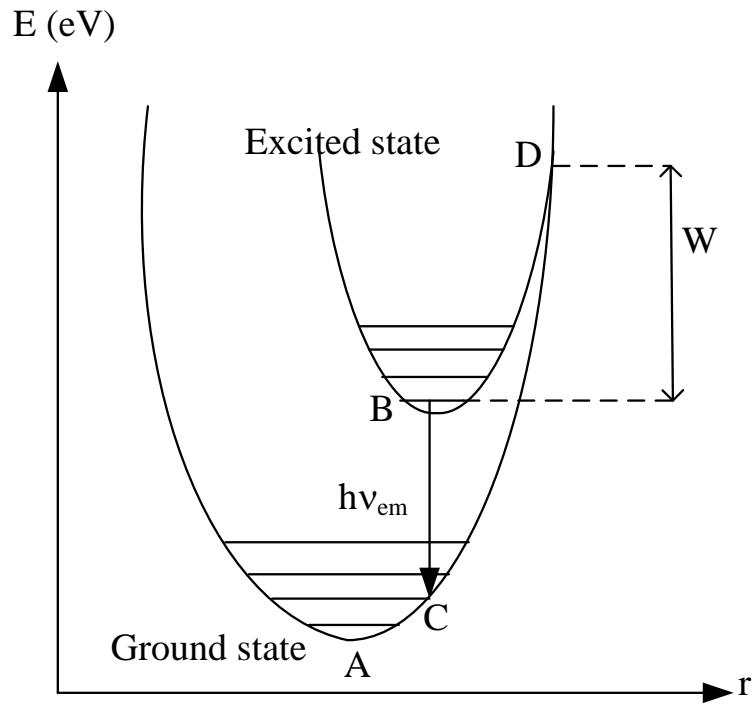


Fig 2

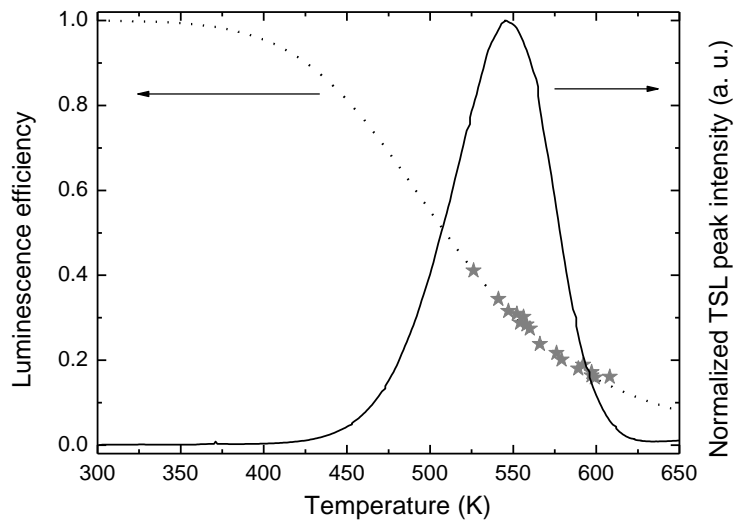


Fig 3

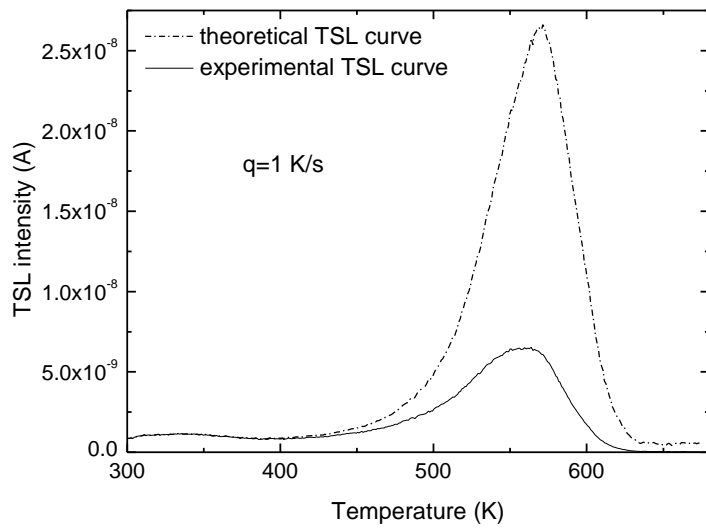


Fig 4

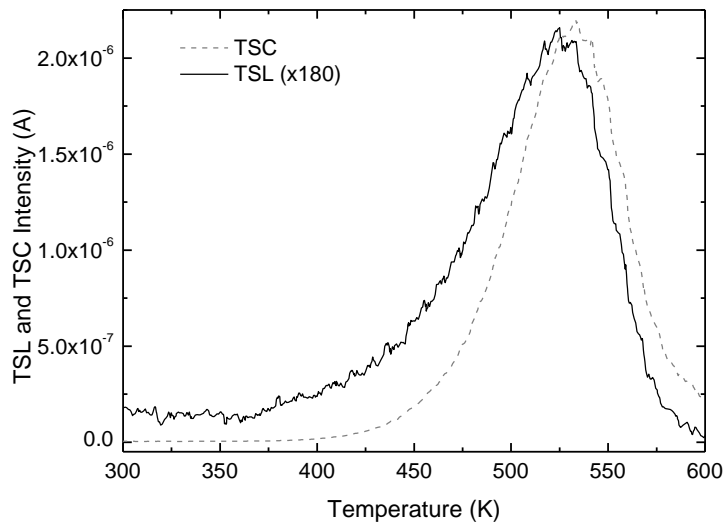


Fig 5