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# Thermally stimulated properties of CVD diamond films

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## Abstract

Thermally stimulated luminescence (TL), current (TSC) and exoelectronic emission (TSEE) of different CVD diamond films grown on silicon substrates have been studied in order to obtain information on defects created during the growth and which induce levels within the gap. TL and TSC have been performed between 100 and 600 K, whereas TSEE has been measured from 300 to 700 K. Several TL peaks located between 275 and 540 K are observed, with different relative intensities depending on the samples. A single TL peak located at about 515–540 K is associated with a trap level 0.8 eV deep. This level gives rise to TSC, whereas the peak located at 275 K, and which may be attributed to the presence of boron, does not give a TSC signal. A TSEE peak located at 595 K is measured for all the samples but cannot be correlated with TL and TSC peaks. This is probably due to the presence of defects that are present only near the surface of the films. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Characterization; CVD; Defect; Diamond films

## 1. Introduction

Because of the development of the chemical vapor deposition (CVD) techniques, CVD diamond films may find a lot of applications in several fields, such as high temperature electronic applications [1], where usual semiconducting materials are prohibited because of their poor chemical and physical properties, or radiation dosimetry [1,2]. They exhibit properties similar to that of natural diamond, but its polycrystalline structure, as well as the impurities incorporated during the growth, involve the presence of relatively high densities of defects that are optically and electrically active. These latter are characterized by deep levels within the gap, which is 5.5 eV, and carriers trapped on these levels at room temperature are frozen. By heating the semiconductor, after the traps were filled (e.g. with a light source), carriers can be emitted from the trap level to the valence or the conduction band and then retrapped on another level. The electronic transitions are here thermally stimulated. Three resultant phenomena can be detected as a function of temperature: thermoluminescence (TL), which is the emission of photons; thermostimulated current (TSC), which is the variation of the electrical conductivity induced by detrapping; thermostimulated exoelectronic emission (TSEE), which is the collection of the electrons that can be released to the vacuum from the surface. The presence of a thermally stimulated peak at a given temperature will give information about the energy level and the density of the defects that are present in the films.

In the present work, CVD diamond films grown with different operating conditions are studied with the three techniques, and the thermally stimulated properties are compared and analyzed to obtain information on the defects involved.

## 2. Experiments

All the samples were grown by hot filament CVD (HFCVD), using a Ta filament, on single crystal Si (100) substrates that were abraded manually, using 1–3 μm diamond grit, prior to deposition. Two sets of samples, called M and R, deposited in different reactors, were studied. The operating conditions of the growth are reported in Table 1. These samples have been characterized by Raman spectroscopy and scanning electron microscopy and the detailed results are described elsewhere [3]. A brief description of the morphology of the films is given in Table 2.

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Table 1
Description of the growth conditions

| Sample | Substrate | $T_{\mathrm{subs}}$ (K) | $T_{\mathrm{filament}}$ (K) | Pressure (kPa) | Gas flow (sccm) | $CH_4$ (%) | $N_2$ (%) |
|---|---|---|---|---|---|---|---|
| M1 | boron-doped Si | 1173 | 2400 | 2.63 | 200 | 0.5 | 0 |
| M2 | boron-doped Si | 1173 | 2400 | 2.63 | 200 | 1 | 0 |
| M3 | boron-doped Si | 1173 | 2400 | 2.63 | 200 | 0.4 | 0 |
| R1 | undoped Si | 1173 | 2500 | 2.63 | 120 | 1 | 0 |
| R2 | undoped Si | 1173 | 2500 | 2.63 | 120 | 1 | 0.02 |

Table 2
Description of the CVD diamond films

| Sample | Structural description | Thickness (μm) | Mean grain size (μm) |
|---|---|---|---|
| M1 | polycrystalline, mixture of 111 and 100 grains | 2–3 | 1 |
| M2 | polycrystalline, mixture of 111 and 100 grains | 3–4 | 0.5 |
| M3 | polycrystalline, mixture of 111 and 100 grains | 2 | 1 |
| R1 | polycrystalline, mixture of 111 and 100 grains | 4 | 1.5–2.0 |
| R2 | polycrystalline, mixture of 111 and 100 grains | 10–11 | 2.0–2.5 |

For all experiments, each sample was previously submitted to UV illumination with a deuterium lamp ORIEL G03 (50 W) covering the entire 200–400 nm spectral range. The temperature irradiation was 77 K for TL and TSC, and 300 K for TSEE. The exposure time was fixed at 5 min, which was enough to reach the saturation of the TL intensity of the samples. The detection of the TL is achieved under secondary vacuum ($10^{-3}$ Pa) between 250 and 600 nm by means of a photomultiplier. The TSC was measured under secondary vacuum ($10^{-3}$ Pa) by applying a bias of 10 V. TSEE recording was obtained under $CH_4$ with the help of a $CH_4$ gas flow counter supplied with a 2450 V voltage. A preliminary experiment of TSEE using a system working under ultra-vacuum ($2 \times 10^{-6}$ Pa) ensured that adsorbed species were not responsible of the TSEE observed, since the signal is similar under vacuum or $CH_4$ flow. After illumination, the films were heated with a rate of 0.5 K $s^{-1}$ for the acquisition of TL, TSC and TSEE response. The accuracy of the temperature position of the peaks is about ±5 K.

## 3. Results and discussion

### 3.1. Excitation and emission response of TL

A preliminary study showed that wavelength excitation is higher than 230 nm, giving evidence that the excitation mechanism for all the phenomena discussed below is a band-to-band transition. Moreover, the spectral analysis of the emission TL of samples M

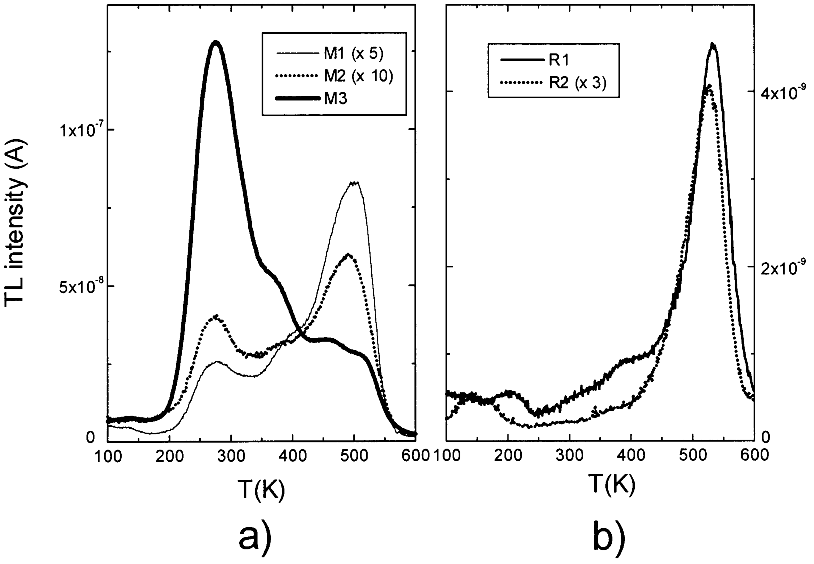

Fig. 1. TL curves of the five CVD diamond films after UV illumination ($D_2$ lamp) in air: (a) samples M and (b) samples R.

showed that it is a single broad band around 2.5 eV, usually called 'band-A'. This band has already been attributed to an electron–hole recombination at a donor–acceptor pair [4].

### 3.2. *Thermally stimulated spectra*

#### 3.2.1. *TL results*

The TL curves of the five films studied are reported in Fig. 1. For the samples M1, M2 and M3, the TL glow curve extends over a range of temperature from 200 to 550 K. The TL curve of sample M3 is constituted of at least four peaks, at positions 275, 380, 475 and 515 K. It is noteworthy that the relative intensity of the 275 and 515 K peaks changes significantly from one film to another, particularly between M1 and M3. If the shapes of M1 and M2 are similar the latter gives a lower signal, even though it is thicker (see Table 2). This can be explained by the half size of the grains (see Table 2), since the grain size is a limiting factor of the TL intensity. The samples R exhibit a glow curve constituted of a main peak located at 540 K and a smaller one at about 385 K, but do not give a significant TL signal at 275 K. The temperature shift observed between the high-temperature peak of the films M1 and those of the films R can be justified by the use of different silicon substrates for each set (difference of thickness and thermal conductivity). In the following discussion, we consider that these TL peaks are induced by the same kind of trap. The presence of the peak at 275 K for samples M is the main difference with samples R. A peak located at about 250 K is currently observed by TL or TSC in boron-doped diamond and is usually related to residual or intentional boron, the boron level being then found at 0.37 eV [5]. Since, in contrast to films R, films M are deposited on a boron-doped silicon substrate, we can assume that the TL peak discussed is related to the presence of boron, whose diffusion has probably occurred from the substrate during the growth.

#### 3.2.2. *TSC results*

TSC experiments were performed on samples M1 and M3. Their TSC glow curves are plotted in Fig. 2 with the TL spectra. In both cases, it is constituted of a main peak located at about 515 K. Its asymmetry suggests the presence of components in the lower temperature range. By taking into account the accuracy of the temperature measurement, we can assume that the 515 K peak is correlated with those observed by TL. Moreover, the film M3 exhibits higher low-temperature components than M1; this, too, might be correlated with the TL measurements, where the signal is higher for the film M3 in the corresponding temperature range. The presence of the 275 K peak is not obvious, even for the sample M3. This suggests that the detrapping process might be localized.

#### 3.2.3. *TSEE results*

The TSEE response is reported for samples M3 and R2 (Fig. 3). It is similar for all the samples and is constituted of a single peak centered around 595 K. A more complete study is proposed elsewhere [6]. Two details led us to consider that this peak is not correlated with the nearest peak observed by TL and TSC. On the one hand, the shape of the glow curve is different since it results from several components for TL and TSC. On the other hand, the shift temperature is too high (55–80 K) between TSEE and the other phenomena to establish a relation between the three phenomena. We showed that this peak is observed only when a surface is well facetted with 100 and 111 faces [6]. This might be explained by a change in the polycrystalline structure near the surface, as observed by Rossi et al. [7] in highly oriented, large-grain diamond films.

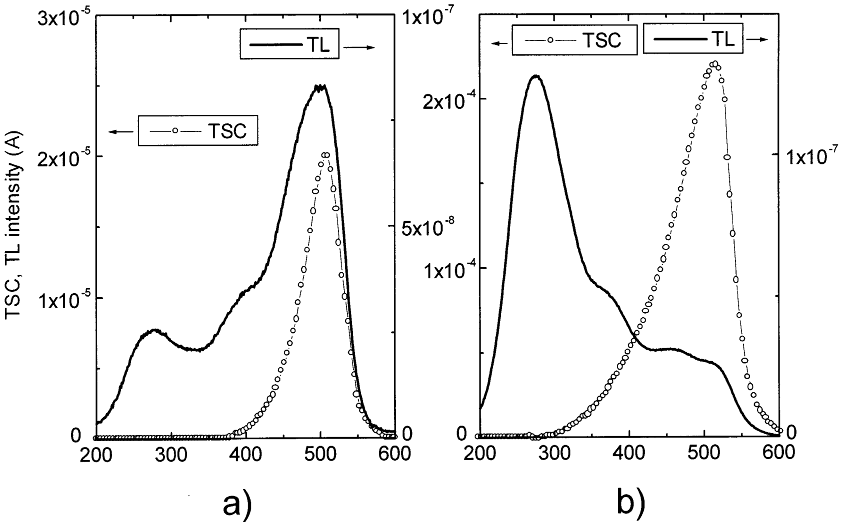

Fig. 2. Simultaneous plot of TL and TSC curves: (a) sample M1 and (b) sample M3.

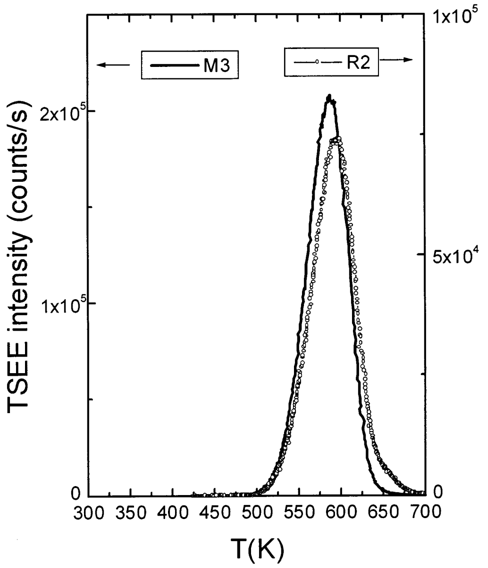

Fig. 3. TSEE curves of diamond films M3 and R2.

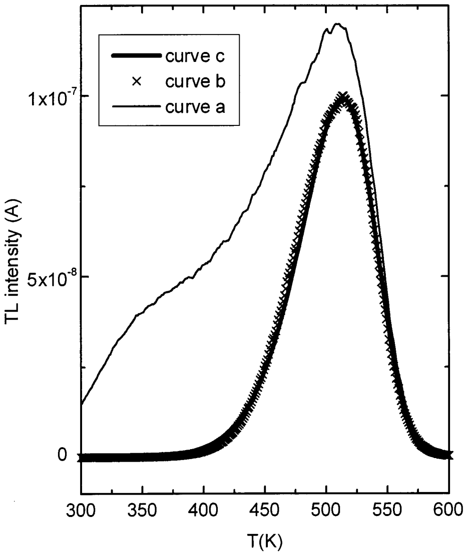

Fig. 4. Experimental isolation and fitting of the single TL peak located at 515 K.

### 3.2.4. *Analysis of the 515 K TL peak*

Since the 515 K peak is observed by TL and TSC, we have focused our interest on the determination of the energy level of the trap involved. To this end, we have experimentally isolated the TL peak for the sample M1. The procedure was as follows: the sample was previously illuminated for 5 min at 300 K then heated up to 423 K to clear the low-energy level traps, and then cooled very rapidly to 300 K. The TL response was then recorded from 300 to 600 K. The TL curves, without (curve a) and with pre-annealing up to 423 K (curve b) are plotted in Fig. 4. The isolated peak was analyzed with three different methods. Chen's method [8] allowed us to attribute a near first-order to the kinetics, i.e. no retrapping occurs. The calculated energy $E$ was 0.75 eV and the frequency factor $s$ was $7\times10^{10}$ Hz. The initial rise method [9] confirmed an energy value of 0.75 eV. We also carried out a numerical fitting developed by Kitis et al. [10] of the peak and the result is reported in Fig. 4 (curve c). This is in good agreement with the experimental curve, and the calculated value of the activation energy is 0.71 eV. A similar treatment was applied to the sample R2, and the results are given in Table 3.

Table 3
Values of the activation energy E of the 515 K TL peak obtained by different methods

| Sample | Chen [8] | | Initial rise [9] | Numerical fitting [10] |
|---|---|---|---|---|
| | $E$ (eV) | $s$ (Hz) | $E$ (eV) | $E$ (eV) |
| M1 | $0.75\pm0.05$ | $7\times10^{10}$ | $0.75\pm0.05$ | $0.71\pm0.05$ |
| R2 | $0.84\pm0.05$ | $3\times10^{8}$ | $0.80\pm0.05$ | $0.84\pm0.05$ |

## 4. Conclusion

From the above discussion, the following has been shown.

(1) TL, TSC and TSEE signals are observed in polycrystalline diamond films having grains with an average size of about 1 μm.

(2) A trap with an energy level at about $0.80\pm0.05$ eV gives rise to a TL and a TSC peak at 515 K.

(3) Under the growth conditions used in this study, boron diffusion occurs in diamond from the silicon substrate, indicated by the presence of a TL peak centered at about 275 K; it does not induce a TSC signal and this suggests that the detrapping process is localized.

(4) The TSEE peak at 595 K does not seem to be correlated with TL and TSC, and results probably from a different structure of diamond close to the film surface.

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