Deep levels and trapping mechanisms in chemical vapor deposited diamond

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Detector-grade undoped chemical vapor deposited (CVD) diamond samples have been studied with thermally stimulated currents (TSC) and photoinduced current transient spectroscopy (PICTS) analyses in the temperature range 300–650 K. Two previously unknown defects have been identified, characterized by activation energies $E_1 = 1.14$ eV and $E_2 = 1.23$ eV, cross sections of about $\sigma \approx 10^{-13}$ cm$^2$ and concentrations of $N_t \approx 10^{16}$ cm$^{-3}$. They have been clearly observed by PICTS and isolated in TSC measurements by use of a fractional annealing cycle in the temperature range 300–400 K. Due to their trap parameters, in particular the high cross section, the levels corresponding to $E_1$ and $E_2$ are characterized by capture times of the order of 10–100 ps. A dominant TSC peak observed at $\approx 500$ K has been also investigated and has been resolved into four components with activation energies of the order of 1 eV and cross sections in the range $10^{-19}$–$10^{-17}$ cm$^2$. Three of these levels exhibit a fast capture rate (0.1–10 ns) in spite of their small cross sections, due to their high concentration in the investigated sample. Correlating our results with room temperature charge collection studies, we propose that the observed traps with their fast capture rates can be effective in limiting the carrier lifetimes and, consequently, the charge collection efficiency of CVD diamond particle detectors © 2002 American Institute of Physics. [DOI: 10.1063/1.1461891]

I. INTRODUCTION

In the development of future high energy physics experiments at the large hadron collider (LHC) under construction at CERN, and in particular at the compact muon solenoid (CMS) and a toroidal apparatus, (ATLAS) one of the crucial problems is the design and production of radiation-hard position-sensitive detectors. These detectors have to be placed at the smallest possible radii and in the very forward tracker region, where hadron fluences of up to $10^{15}$ cm$^{-2}$ are anticipated after 10 years of operation. Diamond has been proposed as an ideal detector material for this environment due to its high radiation hardness, motivating studies of tracking detectors fabricated from polycrystalline chemical vapor deposited (CVD) undoped diamond. In addition to radiation hardness, diamond has properties favorable for charge particle detection: very low leakage current, a low dielectric constant, high electron and hole mobilities, a high saturation velocity, and a long radiation length. In the development of future high energy physics experiments at the large hadron collider (LHC) under construction at CERN, and in particular at the compact muon solenoid (CMS) and a toroidal apparatus, (ATLAS) one of the crucial problems is the design and production of radiation-hard position-sensitive detectors.

Major drawbacks for the use of diamond as a particle detector are the large energy necessary to create an electron-hole pair (13 compared to 3.6 eV for silicon), and the highly defective bulk, which strongly affects the charge collection distance (ccd) of the device. As a figure of merit of the detection efficiency, the ccd is defined as the average distance that electrons and holes generated by the ionizing radiation can drift under the influence of the external electric field before being trapped by deep levels. The ccd is related to the carrier lifetimes, which is limited by defects inside the band gap acting as recombination and trapping centers. In the case where the charge collection time is larger than the carrier lifetime, the charge collection distance is smaller than the detector thickness, and the detector is less efficient than optimal.

Based on transient photocconductivity measurements on Ia natural diamond samples, a model for the trapping in diamond has been proposed, in which the carrier lifetimes are coupled to a nitrogen level acting as a recombination center. The single substitutional nitrogen behaves as an electrical donor with ionization energy around 1.7 eV. The A aggregate (a substitutional pair of N atoms) is believed to act as a very deep donor with ionization energy of about 4 eV. According to this model, typical diamond samples with a nitrogen density of 20 ppm have a limited ccd (from 20 to 50 $\mu$m). To overcome this limitation, it is necessary to use a material with a nitrogen concentration orders of magnitude lower than that of natural diamond. Polycrystalline CVD diamond has shown a remarkable quality improvement in recent years and prototypes of particle detectors based on this material are presently tested by the RD42 CERN collaboration and other groups. Large area, nitrogen-free, polycrystalline diamond planar disks of about 10 cm diameter can be produced at present with mechanical, thermal, and optical properties and electrical resistivity comparable or even superior to natural diamond. The material.

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can be grown in a columnar structure to thicknesses in excess of 500 μm with increasing grain size, starting with small grains (∼1 μm) on the nucleation side to 100 μm sized grains on the growth side. Materials with a ccd of up to 250 μm are now being produced, by thinning the samples from the nucleation side in order to remove the smaller grains. To further increase the ccd, the sample can be irradiated with a β-source up to a dose of about 1 krad to partially passivate the deep traps in the material bulk: this leads to a ccd improvement of 100% or more. Nonetheless, even in the best-quality undoped CVD diamond films, the lifetime of the carriers can be estimated to be of the order 1 ns (considering a ccd of 250 μm and a saturation velocity of about 2.2 × 10^7 cm/s). This illustrates that transport processes in the device are strongly affected by trapping and recombination at the deep levels. The goal for further improvements in the material is to obtain a large-scale tracking device with a signal-to-noise ratio of about 15-to-1 for fast signal collection (compatible with the 25 ns spill structure of the LHC accelerator). A mean signal-to-noise ratio of 10-to-1 has been achieved with microstrip sensors of limited length.

A condition for the improvement in the ccd is a thorough understanding of the charge collection properties of CVD diamond particle detectors, which translates into a major effort to study in detail the distribution of deep levels. In the past, the following methods have been used to extract information about deep energy levels in CVD diamond: dark conductivity,\textsuperscript{17–19} electroluminescence,\textsuperscript{20} transient photocurrent,\textsuperscript{7–8,21–23} photoconductivity (PC),\textsuperscript{24,25} however, only thermal spectroscopy techniques allow to determine simultaneously the activation energies \(E_\text{t}\) and capture cross sections \(\sigma\) of the traps. These experiments include thermally stimulated currents (TSC), thermoluminescence (TL), and several techniques based on transient analysis such as charge-deep level transient spectroscopy (Q–DLTS), capacitance-deep level transient spectroscopy (DLTS), and photoinduced current transient spectroscopy (PICTS),\textsuperscript{26} respectively. In particular, the thermal spectroscopy techniques based on the measurement of currents are suitable to study both doped samples in the form of \(p–n\) or Schottky junctions and insulating materials with ohmic contacts as well. The excitation over the band gap is usually accomplished by an UV\textsuperscript{27} or x-ray source,\textsuperscript{28} or by irradiation with beta particles.\textsuperscript{29} In the many studies found in the literature, one or more of these thermal spectroscopy techniques has been used in the investigation of boron-doped CVD diamond,\textsuperscript{30–32} and undoped CVD diamond.\textsuperscript{8,23–29,30–37} In some of these works, the capture cross section \(\sigma\) has been calculated explicitly, while in other cases it can be deduced either from the activation energy and the glow curve peak position, or from the TL frequency factor \(s\). However, in general, values of \(\sigma\) deduced solely from a single experimental technique have a large systematic uncertainty, because spectra are composed of many overlapping deep level contributions, and thus can be explained by different sets of pairs of parameters \((E_\text{t}, \sigma)\).

For this reason, as suggested previously,\textsuperscript{38,39} we propose to determine the population of deep energy levels by requiring that they explain simultaneously the spectra obtained with different techniques, such as TSC and PICTS. The present article describes such a detailed study on the deep-level distribution in undoped CVD diamond detector-grade films, where we combine TSC and PICTS analyses to obtain a reliable evaluation of the parameters of relevant traps in the energy range 0.3–1.5 eV. Activation energies and capture cross sections have been determined quantitatively from PICTS spectra; these results have been subsequently checked and refined until consistency with TSC spectra has been achieved. Finally, the TSC measurements under trap saturation condition have been used to evaluate the defect concentrations. At the end of the process, the results have been combined to determine which of the detected defects may be relevant in affecting the carrier lifetime and the ccd.

II. EXPERIMENTAL PROCEDURE

A. Material and electrical sample characterization

Our study has been carried out using a commercial undoped CVD diamond film with thickness \(W = 608 \mu\text{m}\), area \(A = 1.0 \times 1.0 \text{ cm}^2\) and with preferred (110) orientation on the growth side, as determined by x-ray diffraction. Both surfaces have ohmic contacts of 5 mm diameter, made by evaporating chromium and gold.

The \(I–V\) characteristic of the sample exhibits an ohmic behavior in the range ±100 V, with a resistivity of about 2 × 10\(^{11}\) \(\Omega\) cm. After UV excitation, the \(I–V\) curve becomes slightly nonohmic, due to polarization effects at room temperature.

The Raman quality of the sample has been assessed with a \(\mu\)-Raman setup at the European Laboratory for Non Linear Spectroscopy (LENS), Florence, using an Ar laser with a green line of 514.5 nm with a power of 50 mW at the sample. The spatial resolution was of the order of 1 μm and the wave number resolution was of the order of 0.1 cm\(^{-1}\). The luminescence background was evaluated by examining a broad wave number interval ranging from close to the laser emission, at about 19 000 cm\(^{-1}\), to about 12 000 cm\(^{-1}\), and was found very low. No luminescence defects were observed in this range. A Raman spectrum of the sample is shown in Fig. 1. The full width at half maximum (FWHM) of the 1332 cm\(^{-1}\) Raman line of diamond decreases slightly from 2.6 to 2.3 cm\(^{-1}\), when evaluated at the substrate and the growth side, respectively, and is comparable to that of natural diamond.\textsuperscript{40} No indication of \(sp^2\) bonding has been observed\textsuperscript{41} in the range 1300–1700 cm\(^{-1}\). The sample had not been polished on the growth side, where a clear faceting was revealed by scanning electron microscope (SEM). The average grain linear dimension is about 20 μm. Figure 2 is a SEM micrograph showing details of the sample growth side, with clearly visible twin planes.

The charge collection distance ccd of the sample was determined by measuring the charge collection efficiency for beta rays of a collimated 74 MBq \(^{90}\)Sr source at NIKHEF (Amsterdam).\textsuperscript{42,43} A scintillator readout by a photomultiplier tube was located downstream of the sample to serve as the trigger, counting at about 0.7 kHz, and to allow the selection of close to minimum ionizing particles (MIPs). The combination of trigger and collimator ensured that all \(\beta\)s recorded traversed the sensitive region of the diamond detector. The
charge signal from the sample was amplified by an Amptek A225 amplifier with a shaping time of 2.4 μs and recorded by a DAQ system. The electronic noise of the system was 350 electrons. The sample exhibited a very slight pumping effect due to the exposure to the β source, and the spectra were reproduced to about 2%. The measured spectra of about 5 K events were fitted by a Landau curve convoluted with a Gaussian to account for the electronic noise of the preamplifier. Figure 3 shows the most probable value of the recorded spectra as a function of applied bias up to a field of $F = 1 \text{V/μm}$, a value close to the saturation field. Using a carrier generation rate of 36 pairs/μm, we obtain, for the observed maximum collected charge of 3500 electrons, and a ccd of about 96 μm.

### B. Experimental setup

Both PICTS and TSC experiments are performed in the temperature range from room temperature up to 650 K, using the same vacuum system and the same excitation lamp. The sample is mounted on a copper plate, very close to a Pt100 platinum temperature sensor, inside the vacuum chamber, where a pressure lower than $10^{-3}$ Torr is maintained by a pumping station. The plate is heated by means of a planar resistance. A detailed description of the vacuum system is given in Refs. 45 and 46.

The sample excitation is provided by a xenon lamp, pulsed at a frequency of 100 Hz, which generates pulses of 0.1 J. The FWHM of the optical pulse is about 2 μs. The emission spectrum cover the range of wavelength between 200 and 1000 nm, with a peak at 300 nm. The lamp is placed a few centimeters from the sample, illuminating the whole sample surface through a UV grade quartz viewport.

The complete PICTS experimental setup is shown in Fig. 4. The sample is dc biased with a Keithley 6517A high-voltage source. The lamp activity is monitored with a fast photodiode with 1 ns rise and fall times (Lasertech ET2010), which triggers the oscilloscope (Tektronix TDS202D). The current transients generated by the pulsed light across the sample are measured using an appropriate readout circuit which converts the current into voltage ensuring at the same time adequate values of transresistance ($150 \times 10^3$ V/A), input resistance (2.2 kΩ) and bandwidth (1 MHz). The readout circuit clamps the photocurrent peak, which is superimposed on the current emitted by the deep levels, in order to avoid the saturation of the oscilloscope input circuit. The entire experiment is controlled by a personal computer, which samples the transient current signal and the temperature. During each temperature sweep, five samples of the current signal are acquired.

![FIG. 1. Raman spectrum of the diamond sample under investigation.](image1)

![FIG. 2. Scanning electron micrograph of the growth side of the sample, showing details of the grains. The size of micrograph is 60×40 μm.](image2)

![FIG. 3. S curve of the of the most probable electron number vs bias field in the range ±1 V/μm. The measurements taken both in the pumped and unpumped state are plotted.](image3)

![FIG. 4. Experimental setup of the PICTS system.](image4)
transient are acquired for each temperature step of 1 K and properly averaged. In addition the computer regulates the heater bias in order to maintain a constant heating rate ($\beta < 0.1$ K/s), slow enough not to affect the shape of the spectrum. The bias $V_{\text{bias}}$ applied to the sample during PICTS measurements is chosen between 10 and 50 V, depending on sampling times, in order to maximize the signal-to-noise ratio.

In TSC experiments, the same voltage source is used to bias the sample and to read the thermally stimulated current at the applied voltage of $V_{\text{bias}} = 100$ V. The traps are filled by exposing the sample to the Xe lamp flashes for several minutes before starting the heating scan with a constant heating rate $\beta = 0.1 - 0.15$ K/s.

**III. EXPERIMENTAL ANALYSIS AND DATA TREATMENT**

### A. Photoinduced current transient spectroscopy

To briefly discuss the PICTS analysis used in this study, let us consider a hole trap, with activation energy $E_i$ and concentration $N_i$. The photoinduced current density transient generated at a fixed temperature $T$ is given by

$$J(T, t) = q \mu_h \tau_h F \eta(T) p_i(0) \exp(-E_i/kT),$$

where $q$ is the electron charge, $\mu_h$ is the hole mobility, $\tau_h$ is the hole lifetime, $F$ is the electric field (assumed to be constant across the sample), $p_i(0)$ is the concentration of traps filled with holes at the initial time $t = 0$. The hole emission coefficient $e_h$ is

$$e_h(T) = \gamma T^2 \sigma_h \exp(-E_i/kT),$$

where $\gamma$ is Boltzmann’s constant and $\sigma_h$ is the capture cross section. The constant $\gamma$ depends on Planck’s constant, $h$, the conductivity effective mass $m^*_c$, and on the number of maxima of the valence band mass $M_v$ as

$$\gamma = 2 \sqrt{3} M_v (2\pi)^{3/2} k^2 m^*_c h^{-3}.$$

Equation (1) describes the trap discharge in an ohmic sample. We observed that the $I$--$V$ characteristic of this sample is only slightly influenced by trap filling if $V_{\text{bias}} < 100$ V, which is an indication that Eq. (1) can be used to describe the process in good approximation. If the trap is known to collect electrons instead of holes, the adequate values of mobility, lifetime, effective mass, and minima of the conduction band must be used in Eqs. (1)–(3).

The ionization energies determined from PICTS analysis are always related to the emission of traps into the closest band. However, both electron and hole emissions give a current flowing in the same direction; thus PICTS cannot be used to distinguish between electron and hole traps.

Several methods can be employed to analyze the PICTS current transient. Muret et al., in their PICTS experiments on boron doped samples with Schottky junctions, used a procedure based on the Fourier analysis of current transients. In his work on IIb natural diamond, adopted two points Lang analysis. However, in samples with a junction, the factor $\mu \tau F$ of Eq. (1) is replaced by half the depletion depth $x_d/2$, which can be taken as constant with temperature if the shallow level concentration is much higher than the deep level concentration. In the case of bulk samples, the generally unknown temperature dependence of $\mu \tau$ may heavily affect the current transient. In the studies carried out in the past by our group, it was assumed that $\mu \tau F$ equals half the charge collection distance $\mu \tau F = c \eta d/2 = \text{const}$, thus neglecting lifetime and mobility variations with temperature. In addition, in order to establish consistency between the results of the PICTS and TSC analysis, two different deconvolution techniques were adopted. In this work we preferred to use a more rigorous “four-points” processing method, which is not influenced by $\mu(T) \tau(T)$ variations with temperature. In such an analysis the PICTS spectrum $S(T)$ is conveniently defined as

$$S(T) = \frac{J(t_1) - J(t_2)}{J(t_0) - J(t_3)}.$$

A spectrum defined in this way does not depend on mobility and carrier lifetime. Because the trap concentration cancels out in Eq. (4), this expression cannot be used to estimate deep level concentrations. It should be noted that saturation of the traps is not usually achieved by the short-pulse periodic excitation used in PICTS measurements, and that in general PICTS is not reliable in estimating defects concentration. If $t_3 > t_2 > t_1 > t_0$ and $t_3 \gg t_0$, the spectrum $S(T)$ takes the form

$$S(T) = \exp[e_h(t_1 - t_0)] - \exp[e_h(t_2 - t_0)].$$

The function $S(T)$ peaks at the temperature $T_p$ for which

$$\frac{1}{e_h(T_p)} = \tau_{\text{ref}} \ln \frac{t_2 - t_1}{t_3 - t_0}.$$

The latter two formulae are analogous to those employed in capacitance DLTS; consequently $E_i$ and $\sigma$ can be determined by measuring many peak positions corresponding to different values of $\tau_{\text{ref}}$, and plotting these points in an Arrhenius plot $\ln(T_p^2 \tau_{\text{ref}})$ vs $(1/T_p)$. The points will lie on a straight line with slope $E_i/k$, which crosses the vertical axis at $\ln(\gamma \sigma)$.

The present uncertainty in the values of some of the physical constants governing the electrical conduction in polycrystalline diamond introduces systematic errors in analyzing the spectroscopic PICTS spectra. Moreover, one has to decide if the traps emit electrons or holes, in order to choose the proper values for the effective mass and the density of states. At this stage of the investigation, the choice is quite arbitrary. Following the example of many authors, who have invoked states near the valence band to account for photoconductivity measurements, we consider hole traps in the dark conductivity, Q-DLTS, we consider hole traps in the same direction; thus PICTS cannot be used to distinguish between electron and hole traps.
denced for example by the large spread in the combined electron-hole mobility reported in the literature,\textsuperscript{52} ranging from 50 to 4000 cm\textsuperscript{2}/V s.

**B. Thermally stimulated current**

Under the same assumption as in the last section, the TSC spectra is given by

\[
J(T) = q \tau_b F \mu_b \rho_s(0) e_b(T) \exp \left( -\frac{1}{\beta} \int_{T_0}^{T} e_b(T') dT' \right),
\]

where \(\beta\) is the heating rate, assumed to be constant during the temperature scan, and \(T_0\) is the initial temperature. In the TSC analysis it is not possible to eliminate the temperature dependence of \(\mu_b \tau_b\), and we assumed \(\mu_b \tau_b F = \text{ccd}/2\). The ccd was estimated experimentally from charge collection measurements made at room temperature, thus neglecting the temperature dependence of lifetime and mobility. The TSC peak position \(t_{TR}^c\) is related to the heating rate \(\beta\) and to the trap parameters.\textsuperscript{54}

**C. Charge collection efficiency and charge collection distance**

The basic phenomenon limiting the lifetime of excess carriers which is usually invoked to explain charge collection efficiency (cce) measurements is the recombination through deep centers. In this case, the rate equation governing the carrier lifetime (e.g., of holes) reduces to

\[
\frac{dp}{dt} = -\frac{p}{\tau_h}.
\]

Here \(p\) is the hole density in the valence band, and \(\tau_h\) is the characteristic hole lifetime. This equation holds strictly locally, and for macroscopic measurements, the quantities in it are averages over the entire sample. In this case the contribution of the trap centers to the limited value of cce and ccd are connected by Hecht’s formula.\textsuperscript{53} If the electric field and the initial carrier generation are uniform across the sample, the charge collection efficiency cce, i.e., the ratio of collected and generated charge, can be expressed as

\[
\text{cce} = \frac{Q}{Q_0} = \frac{\tau_e}{\tau_{TR}} \left[ \frac{1 - \frac{\tau_e}{\tau_{TR}}} {1 - \exp \left( -\frac{t_{TR}}{\tau_e} \right)} \right] + \frac{\tau_h}{\tau_{TR}} \left[ 1 - \frac{\tau_h}{\tau_{TR}} \frac{1 - \exp \left( -\frac{t_{TR}}{\tau_h} \right)} {1 - \exp \left( -\frac{t_{TR}}{\tau_h} \right)} \right].
\]

Here \(t_{TR}^c = W/(\mu_{e,h} F)\) are the transit times across the thickness \(W\) for the electrons and holes, respectively. The relationship between lifetime and ccd is \(\text{ccd} = \text{ccd}_e + \text{ccd}_h = (\mu_e \tau_e + \mu_h \tau_h) F\). The two terms on the right hand side of Eq. (9) are due to the contributions from electron and hole motion, respectively. In the limit of long lifetimes each of these terms approaches the value 0.5, as \(0.5 \times (1 - t_{TR, c}^e 3 \tau_e)\), leading to full charge collection. On the other hand, for short life times, i.e., \(\text{ccd} \ll W\), each term gives a contribution equal to \(\tau_{e,h} t_{TR, e}^c\) and in this limit \(\text{ccd} = \text{ccd}/2W\). Thus, a significant reduction in the cce is expected for lifetimes \(\tau_{e,h}\) comparable or smaller than the transit time. The rate equation for a hole trap is

\[
\frac{dp}{dt} = N_i(e_e + c_h) - p_e(c_e + e_h + e_e + c_h),
\]

where \(N_i\) is the total trap concentration, while \(c_e = \sigma_e(v_e)n\) and \(c_h = \sigma_h(v_h)p\) are the capture coefficients for holes and electrons, respectively. \(n\) is the electron density in the conduction band and \(\langle v_{e,h} \rangle\) is the carrier thermal velocity. The steady state trap occupation, for the case that free carrier concentrations can be considered constant in time, is given by

\[
p_e(\infty) = \frac{e_e + c_h}{e_e + c_h + e_h + c_e}.
\]

The general problem of a trap interacting with carriers through the capture and emission process cannot be solved analytically. Several semianalytical expressions can be found in Ref. 54. However a useful relationship can be obtained if (i) the only process limiting the carrier lifetime is the capture by the trap of a single species (i.e., holes) and (ii) at any time, \(p_e \ll N_i\). In this case, Eq. (10) reduces to

\[
\frac{dp_e}{dt} = -\frac{dp}{dt} = \sigma_h(v_{h}) N_i p_e.
\]

Under these assumptions the emission process is uncoupled from capture, being much slower, and an estimate of the time scale of emission is \(\tau^e = 1/\sigma_e(v_e)\).

Expression (12) is formally identical to Eq. (8) if the hole lifetime is set equal to the capture time constant \(\tau_e\), defined as

\[
\tau_e = \frac{1}{N_i \sigma_h(v_h)}.
\]

This implies that:

(i) the fastest rate at which a trap can limit the charge collection is given by its capture time constant and

(ii) a trap can affect the charge collection only if its trapping time is shorter than the transit time.

In our sample, the hole transit time in our sample is \(t_{TR} = 6\) ns for a saturated drift velocity, thus a trap can be responsible for the reduction of cce only if log(\(\sigma\)) + log(\(N_i\)) >1.9.

Note that in particle detectors, where the charge is generated by ionizing particles, the pair generation occurs only in a small volume along the particle trajectory and, strictly speaking, the nonequilibrium excess carrier concentrations \(n\) and \(p\) cannot be defined. However, the predictions of Eq. (12) agree with more sophisticate Monte Carlo simulations\textsuperscript{55,56} and with experiments.\textsuperscript{57} Thus, the earlier equations can be used to study the charge collection after a single local event, such as a MIP crossing the detector.

**IV. EXPERIMENTAL RESULTS**

**A. PICTS**

PICTS measurements have been performed in the temperature range 290–650 K, in order to sample the current signal \(J(t)\) at different times \(t_i\) in the range 20–4500 \(\mu\)s. The
corresponding values of $\tau_{\text{ref}}$ vary between 10 and 1200 $\mu$s. Twenty quadruples of sampling times have been selected in order to build up the PICTS spectra $S(T)$ defined by Eq. (4) and find the dominant spectral contributions. A few of these spectra are shown in Fig. 5. The general conclusion of this analysis is that a large number of emissions contribute to form these broad spectra. However, in our temperature range, three peaks can be identified, which can be associated with three dominant deep levels (indicated in Fig. 5 as Nos. 1, 2, and 3). The peak positions change with $\tau_{\text{ref}}$, shifting toward higher temperatures as $\tau_{\text{ref}}$ decreases. The Arrhenius plots obtained from these spectra are shown in Fig. 6; each marker corresponds to a different peak. Note that, for certain values of $\tau_{\text{ref}}$, a peak may shift out of the temperature range under observation, or cannot be well identified. We have selected sampling times which help to minimize the overlap of the three spectral contributions. Because a certain amount of overlap persists, we have refined the parameters obtained from the Arrhenius plots with the help of a subsequent deconvolution procedure. The final parameters obtained for the three traps are listed in Table I, together with relevant information obtainable from the trap signatures, namely: capture time $\tau_c$ [defined in Eq. (13)] and emission time $\tau^\text{e}$. The trap concentrations have been deduced from TSC, as explained in the next section. In addition, the predicted TSC peak positions are shown, evaluated for three different heating rates: the rate used by us ($\beta=0.15$ K/s) and, in order to allow an easy comparison with other results, the fastest and slowest heating rates found in the literature ($\beta=0.05$ K/s and $\beta=0.5$ K/s).

The results take into account the uncertainty derived from experimental errors and systematic of the data analysis. In particular the uncertainly in energy position is about 0.05 eV, while the cross sections may have a spread of about one decade around the central value calculated from the Arrhenius plots.

### B. TSC

We performed several measurements with different filling times $T_{\text{fill}}$, ranging from 1 to 30 min. The TSC emissions of the level Nos. 1 and 2 (see Tables I and II) occur in the temperature range 300–400 K. They are almost hidden by other spectral contribution of much higher intensity, thoroughly studied in previous works and discussed in the following section. In order to demonstrate the TSC contributions of the level Nos. 1 and 2, we adopted the following procedure. The filling of the traps by illumination with the Xe lamp was followed first by heating the sample to 410 K, during which a first spectrum was measured. Then the sample was cooled down to room temperature, and, without any further filling, the temperature was ramped up to 650 K, during which a second spectrum was acquired. The results of this procedure are shown in Fig. 7, where two pairs of spectra, corresponding to different filling times, are displayed (curves a and b). The inset in the figure contains a scheme of the annealing procedure.

By subtracting the second spectrum from the first, the TSC contribution of the levels activating near room temperature can be isolated, as shown in Fig. 8. In the same figure, the spectral contributions expected from levels Nos. 1 and 2 are also shown, giving a reasonably good agreement with the

<table>
<thead>
<tr>
<th>Level No.</th>
<th>$E_i$ (eV)</th>
<th>$\sigma$ $(\text{cm}^2)$</th>
<th>$N_i$ $(\text{cm}^{-3})$</th>
<th>$\tau_c$ (ps)</th>
<th>$\tau^\text{e}$</th>
<th>$T_p$ (K)</th>
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<tr>
<td>1</td>
<td>1.14</td>
<td>$4 \times 10^{-13}$</td>
<td>$\sim 10^{16}$</td>
<td>20</td>
<td>$\sim 13$ h</td>
<td>341</td>
</tr>
<tr>
<td>2</td>
<td>1.23</td>
<td>$9.5 \times 10^{-14}$</td>
<td>$\sim 10^{16}$</td>
<td>82</td>
<td>$\sim 76$ days</td>
<td>380</td>
</tr>
<tr>
<td>3</td>
<td>0.39</td>
<td>$3.2 \times 10^{-19}$</td>
<td>...</td>
<td>13 ms</td>
<td></td>
<td>191</td>
</tr>
</tbody>
</table>
shape of the measured signals, even if the presence of other contributions is clearly observable. A long filling time ensures the saturation of the signal level. The trap concentrations can be estimated through the area of the corresponding TSC spectrum, resulting in \( N_t \approx 10^{16} \text{ cm}^{-3} \), as listed in Tables I and II.

We have also checked the saturation condition by performing an additional measurement after sample excitation by \( \gamma \) rays. The sample was exposed to \( \gamma \) rays from a \( ^{60}\text{Co} \) source at a rate of 2 Gy/min, up to a dose of 8.45 Gy, using the facilities of the radiotherapy unit of The Clinical Physio-pathology Department of the University of Florence. The TSC measurement was performed 3 h after irradiation. The results are shown in Fig. 7 (curve c). By comparison with the measurements after excitation with the Xe lamp, it can be seen that the traps activated near room temperature discharged before the start of the measurements. In the range \( 1000/T = 2.2 \text{ K}^{-1} \) the spectrum obtained after \( \gamma \) ray exposure is 2–4 times higher than the spectrum corresponding to strong UV illumination and is peaked towards higher temperature. Further information can be extracted from Fig. 9, where the various TSC spectra are plotted on a linear scale after subtraction of the background current. All the spectra exhibit a broad and clearly structured peak extending between 400 and 600 K, which can be fitted using four peaks, whose parameters are listed in Table III, together with the trap concentrations found after UV signal saturation and \( \gamma \) irradiation, respectively. The concentrations found for level Nos. 4 and 5 are the same in the two cases; the detected concentration of level No. 6 increases by a factor 1.5 after \( \gamma \) irradiation, and the detected concentration of level No. 7 increases by a factor 3.25. Thus, it can be concluded that the light from the Xe lamp is unable to completely fill levels with an energy higher than about 1.2 eV. Finally, we list in Table III the capture time corresponding to the concentration found after \( \gamma \) irradiation, calculated with Eq. (13). The emission time constants have been omitted since they are exceedingly long at room temperature (>10 years).

V. DISCUSSION

A. Deep level content

The dominant peak in our TSC spectra between 450 and 500 K has been intensively studied in the past, in samples similar to ours obtained from previous batches from the same manufacturer. In Ref. 27 it is stated that the main features of the spectrum could be explained by assuming a dominant level with parameters \( (E_t = 1 \text{ eV}, \sigma \approx 10^{-18} \text{ cm}^2) \). Moreover, the contribution of at least other three levels, with energies lying in the range \( E_t \approx 0.5–0.7 \text{ eV} \), cross section \( \sigma \approx 10^{-19}–10^{-22} \text{ cm}^2 \), and total concentration \( N_t \approx 10^{17} \text{ cm}^{-3} \), appeared after an annealing procedure. In Refs. 38 and 39, the fine structure of the deep levels in the 1 eV region was explored, leading to the identification of two levels with parameters \( (E_t = 0.95 \text{ eV}, \sigma = 10^{-19} \text{ cm}^2) \) and \( (E_t = 1.1 \text{ eV}, \sigma = 10^{-18} \text{ cm}^2) \). Their total concentration, measured at trap saturation, was \( N_t = 4 \times 10^{18} \text{ cm}^{-3} \). Similar evidence has been reported in Ref. 34, where a peak at 450 K with a corresponding cross section of \( \sigma \approx 10^{-19} \text{ cm}^2 \) was observed by TSC with \( \beta = 0.2 \text{ K/s} \). Vittone et al.29 found by TL analysis \( (\beta = 8 \text{ K/s}) \) evidence for at least two deep levels in the range \( E_t = 0.98–1.12 \text{ eV} \), \( \sigma \approx 10^{-18}–10^{-19} \text{ cm}^2 \). All

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**TABLE II. Uncertainties on the values of the deep level parameters reported in Table I.**

<table>
<thead>
<tr>
<th>Level No.</th>
<th>( E_t ) (eV)</th>
<th>( \sigma ) (cm(^2))</th>
<th>( N_t ) (cm(^{-3}))</th>
<th>( \tau_c ) (ps)</th>
<th>( T_p ) (K) (( \beta = 0.15 \text{ K/s} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.14 ± 0.05</td>
<td>( 10^{-14}–10^{-12} )</td>
<td>( \approx 10^{16} )</td>
<td>8–78</td>
<td>330–380</td>
</tr>
<tr>
<td>2</td>
<td>1.23 ± 0.05</td>
<td>( 5 \times 10^{-14}–10^{-11} )</td>
<td>( \approx 10^{16} )</td>
<td>15–155</td>
<td>360–410</td>
</tr>
<tr>
<td>3</td>
<td>0.39 ± 0.05</td>
<td>( 10^{-19}–10^{-18} )</td>
<td>···</td>
<td>((7–77) \times 10^6)</td>
<td>175–234</td>
</tr>
</tbody>
</table>

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FIG. 7. TSC spectra as functions of the inverse of the temperature \( T \). The three curves refer to different filling times and different excitations. Curve a: 10 min exposure to the Xe lamp. Curve b: 30 min exposure to the Xe lamp. Curve c: exposure to a \(^{60}\text{Co} \) \( \gamma \) source up to a dose of 8.45 Gy. The annealing step at 410 K is evidence for the level Nos. 1 and 2; clearly visible on a logarithmic scale, notwithstanding the dominant peak at higher temperature. The inset scheme describes the annealing procedure.

FIG. 8. Results of TSC spectra subtraction (heavy lines). The filling times corresponding to the various curves are from top to bottom: 30, 15, 10, 5 min. The expected emissions of the level Nos. 1 and 2 discovered by PICTS are also shown (thin lines).
these observations agree with the identification of the level Nos. 4 and 5 reported in the last section. Yet these two levels alone cannot account for the broad shape of the spectra shown in Fig. 9. We found in fact that two additional level Nos. 6 and 7 were needed for getting a satisfactory fit of the experimental curves. A level very similar to No. 7 with parameters \( E_t = 1.4 \text{ eV}, \sigma = 3 \times 10^{-17} \text{ cm}^2 \), was found by Muret et al.\(^{30} \) by PICTS on boron-doped homoepitaxial diamond. Level Nos. 6 and 7 are also consistent with recent TSC measurements\(^{58,59} \) on heavily irradiated high-quality undoped CVD diamond. In these measurements a shoulder appears on the right side of the dominant peak at the location of our level Nos. 6 and 7. This shoulder is clearly visible after irradiation to a high neutron fluence of \( 10^{15} \text{ cm}^{-2} \), due to the radiation-induced removal of the deep levels Nos. 4 and 5.

In the lower energy range we have identified by PICTS a level with parameters \( E_t = 0.39 \text{ eV}, \sigma = 1.4 \times 10^{-18} \text{ cm}^2 \). In Ref. 38 a distribution of levels in the range \( E_t = 0.4 \text{ to } 0.6 \text{ eV}, \sigma = 10^{-15} \text{ to } 10^{-18} \text{ cm}^2 \) and total concentration \( N_t = 4 \times 10^{12} \text{ cm}^{-3} \) was deduced from consistent TSC and PICTS analyses. The corresponding broad TSC signal \( (\beta = 0.1 \text{ K/s}) \) is peaked at 180 K. A TSC peak at the same temperature was found by Tromson et al.\(^{60} \) using a heating rate of \( \beta = 0.2 \text{ K/s} \); they deduced an energy of 0.3 \text{ eV} using a heating rate method with only two points. A similar result \( (E_t = 0.31 \text{ eV}, \sigma = 1.1 \times 10^{-18} \text{ cm}^2, N_t = 8 \times 10^{13} \text{ cm}^{-3}) \) was obtained by capacitance DLTS using a boron-doped polycrystalline sample.\(^{61} \) Marshall and Walters\(^{22} \) interpreted transient photoconductivity and residual field measurements in CVD diamond to be consistent with various sets of localized states covering the energy range 0.2–0.8 \text{ eV}.

We have detected by PICTS two deep levels, named Nos. 1 and 2, with parameters \( (E_{t1} = 1.14 \text{ eV}, \sigma_1 = 4.3 \times 10^{-13} \text{ cm}^2), (E_{t2} = 1.23 \text{ eV}, \sigma_2 = 9.5 \times 10^{-14} \text{ cm}^2) \). These values are consistent with the TSC observation, which yield an estimated concentration \( N_t \approx 10^{16} \text{ cm}^{-3} \). Note that the parameter spreading reported in Table II would cause the TSC signal of Fig. 5 to be present across the entire temperature range. Thus, the contributions in excess to level Nos. 1 and 2 may be due to a quasi-continuous distribution of states in the range \( E_t = 1 \text{ to } 1.3 \text{ eV}, \sigma = 10^{-12} \text{ to } 10^{-14} \text{ cm}^2 \).

A number of observations in recent years may be related to level Nos. 1 and 2. Tromson et al.\(^{62} \) observed, with TSC in undoped CVD diamond \( (\beta = 0.05 \text{ K/s}) \), a small shoulder of a higher temperature peak, located near 350 K. This could be ascribed to the level Nos. 1 and 2, which emit between 350 and 375 K in our TSC measurements. In addition they found a peak near 390 K \( (\beta = 0.5 \text{ K/s}) \) in natural diamond, and a peak at 375 K in high quality IIa diamond. Similar results on natural IIa diamond\(^{60,62} \) led to the observation of two peaks in the range 300–400 K.

### B. Effect on carrier lifetime

The largest charge collection distance for CVD diamond reported so far in literature\(^{63} \) is cc = 280 \text{ \mu m}. A charge collection efficiency as high as 70% has been reported\(^{55} \) from charge collection measurements using an \( \alpha \) source. The cc can be limited both by recombination and trapping processes. In order for the deep levels to affect the cc measurements they must have a capture time constant shorter or of the order of the transit time \( (t_{TR} = 1 \text{ ns}) \). There is experimental evidence supporting the existence of trapping states with fast capture rates. PC transient measurements performed on natural IIa and CVD diamond\(^{5,7,8,21,25,51} \) reported carrier lifetimes in the range from 40 ps to 1 ns. Reference 25 located a high concentration of hole traps with fast capture rate near the valence band (5 states), in addition to a distribution of deep levels at 1.9–2.1 and 2.8–3.2 \text{ eV} above the valence band maximum.

There are many traps in the energy range up to 1.5 \text{ eV}, which are well identified in CVD diamond by TSC and TL, but none is likely to have a fast capture rate. This is because they all exhibit either a small capture cross section, or an insufficient concentration of traps. It is worth noting at this point that Gonon et al.\(^{18} \) reported a level at 1.86 \text{ eV} with a cross section as high as \( 3 \times 10^{-15} \text{ cm}^2 \); however, an evaluation of the trap concentration is missing in this work. The levels around 1 \text{ eV} reported in the past exhibit capture times ranging from 10 to several 100 ns. Thus, it seems that these levels will have no effect on the cc.
The high temperature features (Nos. 5, 6, and 7) observed in our TSC spectra, correspond to defects exhibiting low capture cross sections ($\sigma \sim 10^{-17} \text{ to } 10^{-18} \text{ cm}^2$) but high concentrations ($N_t \sim 10^{18} \text{ to } 10^{19} \text{ cm}^{-3}$). As a result the trapping times are in the range 0.1–10 ns, using Eq. (13). All these levels should account for the limitation of the carrier lifetime and correspondingly of the ccd. They are often found in CVD diamond, as discussed earlier, but can limit the ccd only if their concentration is very high, as in the present case, because of their small cross section. Concentrations of these levels of one order of magnitude smaller have been found in diamond samples of higher quality. Thus, these levels may limit the ccd, but other traps with a fast capture rate have to exist in order to explain the limitation of the collection efficiency in high-quality samples.

The level Nos. 1 and 2 detected in this work exhibit a capture time constant ranging from tens to hundreds of picoseconds, with a concentration $N_t \sim 10^{16} \text{ cm}^{-3}$; their fast capture rate is mainly due to the high cross section of these traps. These levels may be effective in limiting the ccd in high quality samples.

VI. CONCLUSIONS

Combined PICTS and TSC measurements have been performed on a detector-grade CVD diamond sample exhibiting a mean charge collection distance of about 100 $\mu$m at a field of 1 V/$\mu$m. The sample was excited during PICTS and TSC with a pulsed xenon lamp. By this method we have been able to clearly detect several deep levels in the energy range 0.3–1.5 eV, and determine their trap parameters $E_t$, $\sigma$, and $N_t$. The order of magnitude of the deep level concentration $N_t$ has been determined by measuring the TSC spectrum after trap saturation with gamma irradiation up to a dose of 8.45 Gy using a $^{60}$Co source.

Two new defects, activated close to room temperature (indicated as Nos. 1 and 2) have been clearly observed by PICTS. These defects are not visible in a traditional TSC measurement, being obscured by dominant features at higher temperatures. They have been also detected in this work by TSC with the help of proper fractional annealing stages. Defect Nos. 1 and 2 are characterized by activation energies $E_1 \sim 1.14$ eV and $E_2 \sim 1.23$ eV, respectively, and cross section $\sigma \sim 10^{-13} \text{ cm}^2$ and concentration $N_t \sim 10^{16} \text{ cm}^{-3}$. A dominant TSC peak due to the contribution of four deep levels with activation energies of the order of 1 eV, cross sections in the range $10^{-18} \text{ to } 10^{-17} \text{ cm}^2$ and $N_t \sim 10^{16} \text{ to } 10^{19} \text{ cm}^{-3}$ has been also observed near 500 K.

The determination of the trap parameters of the detected peaks allowed us to evaluate the order of magnitude of the corresponding carrier capture time, which is about 10–100 ps for Nos. 1 and 2, about 100 ns for No. 4, a few nanoseconds for No. 5 and 0.1–1 ns for Nos. 6 and 7, respectively. Since the transit time of the carriers in the sample is of the order of 1 ns we conclude that level Nos. 1 and 2 and, probably to a lesser extent, Nos. 5, 6, and 7 could be effective in limiting the charge collection distance ccd of the device. On the other hand, the long carrier capture time of level No. 4 makes it ineffective in limiting the ccd.

Our results could explain recent observations concerning heavily irradiated CVD diamond films, where a significant removal of defect Nos. 4 and 5 was measured. The neutron irradiation reduced the concentration of the defect Nos. 4 and 5 by more than an order of magnitude, but at the same time the ccd decreased only by 30%.

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