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# Quantitative analysis of electronic absorption of phosphorus donors in diamond

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ABSTRACT

In this work, phosphorus donors in diamond have been investigated by means of Fourier Transform Infra-Red (FTIR) transmission spectroscopy on a series of fully-characterized homoepitaxial layers. Low-temperature FTIR absorption spectra have been obtained for concentrations of donors in the range $N_D = 3.7 \times 10^{16}$– $3.5 \times 10^{18}$ cm$^{-3}$ and compensating acceptor impurities in the range $N_A = 2.3 \times 10^{16}$– $3.0 \times 10^{18}$ cm$^{-3}$. The absorption spectra is shown to exhibit two peaks at 4220 cm$^{-1}$ and 4540 cm$^{-1}$ corresponding to electronic transitions from the ground state to the $2p_0$ and $2p_{\pm}$ excited states, respectively, of phosphorus donors in the neutral state of charge. The intensity of the most intense peak at 4540 cm$^{-1}$ is found proportional to $N_D$-$N_A$ over two decades. The absorption cross-section of the corresponding transition is deduced providing a calibration law for the determination of $N_D$-$N_A$ in phosphorus-doped diamond. Furthermore, the linewidth of the peak exhibits a linear variation with the compensating acceptor concentration, interpreted as the effect of the distribution of ionized impurities. The use of the non-destructive and contact-less FTIR optical method is finally discussed to determine the compensation ratio in phosphorus-doped diamond.

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## 1. Introduction

The n-type conductivity in diamond is presently one of the major issues for electronic applications such as high power devices, UV light emitting diodes, DNA sensors, and electron emitters [1–6]. Up to now phosphorus is the substitutional donor which gives the highest n-type conductivities, despite its high ionization energy of 0.6 eV [7]. Using microwave-plasma-assisted chemical vapor deposition (MPCVD), phosphorus can be incorporated in substitutional sites of the diamond lattice during the growth. Its incorporation remains easier on (111) oriented diamond surfaces than on (100) [8,9] though this surface is preferred for applications. However, both (111) and (100) homoepitaxial layers still suffer from a relatively high compensation of donors by residual impurities and defects [10]. Today, it is striking that the n-type conductivity of phosphorus-doped diamond at room temperature is mainly limited by the problem of compensation rather than by the donor concentration. Up to now, the lowest compensation ratios, defined as $k = N_A / N_D$, ($N_A$ the compensating acceptor concentration and $N_D$ the donor concentration) reported in n-type diamond are ~40% on the (100) orientation [11] and ~5% on the (111) orientation [12], as deduced from electrical measurements. The contrast is striking with p-type diamond doped with boron where the compensation ratio can reach values below one part per million [13].

Evaluating the compensation ratio of phosphorus-doped diamond by Hall effect measurements is not an easy task because of the high resistivity of the films and the high contact resistance of metals on n-type diamond. Cathodoluminescence (CL) spectroscopy has proven [14] to be a powerful optical technique to quantify the concentration of phosphorus incorporated in donor sites, $N_D$. CL is a complementary analysis because it is sensitive to phosphorus atoms in substitutional sites i.e. both compensated and uncompensated ones. In Ref. [14], a relationship is produced to determine $N_D$ by CL. However, under electron-hole pair injection, all acceptors are neutralized. Consequently, the compensation effect is not assessed with CL spectroscopy.

An alternative technique to probe the phosphorus donors in diamond is infrared absorption spectroscopy. It is commonly used for a quantitative analysis of impurity concentrations in semiconductors from the knowledge of the absorption cross-section of electronic or vibrational transitions [15]. For p-type diamond doped with boron, Collins et al. correlated the absorption intensity of the electronic transitions of neutral boron to its concentration and provided calibration curves [16]. In 2000, electronic transitions between the ground state 1s and different excited states of neutral phosphorus atoms were observed by infrared absorption spectroscopy by Gheeraert et al. The authors discussed the photoionization background and related its magnitude to the phosphorus content in the gas mixture during growth [17]. However, the lack of accurate values of $N_D$ and $N_A$ in their samples prevent them to give a more useful calibration law for phosphorus-doped diamond characterization.

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**Table 1**
Sample characteristics. Phosphorus donor concentrations ($N_D$) from SIMS, thickness (d), compensation ratio (k) deduced from electrical measurements and the corresponding concentrations of compensating acceptors ($N_A$) and neutral phosphorus donors ($N_D$-$N_A$ = (1 − k)$N_D$), integrated intensity ($I_A$) and full width at half maximum (Γ) of the 1s → $2p_\pm$ absorption peak. Sample D169b is (100)-oriented. All others are (111)-oriented.

| Sample | $N_D$ ($cm^{-3}$) | d (µm) | k (%) | $N_A$ ($cm^{-3}$) | $N_D$-$N_A$ ($cm^{-3}$) | $I_A$ ($cm^{-2}$) | Γ ($cm^{-1}$) |
|---|---|---|---|---|---|---|---|
| D169b | $3.7 \times 10^{16}$ | 6.30 | 40 | $1.5 \times 10^{16}$ | $2.3 \times 10^{16}$ | 75 | 15 |
| D46 | $6 \times 10^{17}$ | 1.32 | 34 | $2.0 \times 10^{17}$ | $4.0 \times 10^{17}$ | 1777 | 25 |
| D43 | $8.5 \times 10^{17}$ | 1.62 | 34 | $2.9 \times 10^{17}$ | $5.6 \times 10^{17}$ | 3031 | 31 |
| D48 | $9.4 \times 10^{17}$ | 1.46 | 14 | $1.3 \times 10^{17}$ | $8.1 \times 10^{17}$ | 2668 | 23 |
| D42 | $1.7 \times 10^{18}$ | 1.23 | 9 | $1.5 \times 10^{17}$ | $1.5 \times 10^{18}$ | 5160 | 26 |
| D31 | $3.0 \times 10^{18}$ | 1.50 | 35 | $1.1 \times 10^{18}$ | $2.0 \times 10^{18}$ | – | 64 |
| D147 | $3.5 \times 10^{18}$ | 1.12 | 16 | $5.7 \times 10^{17}$ | $3.0 \times 10^{18}$ | 10403 | 44 |
| D166 | $3.5 \times 10^{18}$ | 1.52 | 21 | $7.4 \times 10^{17}$ | $2.8 \times 10^{18}$ | 9500 | 39 |

In this work, we have chosen to focus on the 1s → $2p_\pm$ absorption peak at 4540 $cm^{-1}$ since it is the most intense absorption line associated to the electronic transitions of phosphorus donors in diamond. The infrared absorption measurements have been performed in a series of extensively characterized homoepitaxial layers with different phosphorus doping levels. We demonstrate that the intensity of the electronic absorption of phosphorus donors at 4540 $cm^{-1}$ is proportional to the net donor density, namely $N_D$-$N_A$. We provide a calibration curve for the measurement of $N_D$-$N_A$ by using infrared spectroscopy. We also observe that the linewidth of the 1 s → $2p_\pm$ absorption peak follows a linear dependency on $N_A$. The possible origins of the broadening are discussed. We further evaluate the uncertainty associated to the determination of the compensation from infrared measurements, performed alone or in a combination with other techniques, such as CL or Secondary Ion Mass Spectrometry (SIMS).

## 2. Experiments

The (111) and (100) phosphorus doped homoepitaxial diamond films were grown on HPHT type Ib diamond crystals by microwave plasma assisted chemical vapor deposition (MPCVD). For the (111) orientation, the deposition conditions were described by Kociniewski et al. [18,19]. The D147 and D166 samples are replicas of the D42 sample, with $N_D$ of the same order of magnitude. The (100) oriented sample was grown thanks to the new set of growth parameters we found recently [20].

SIMS experiments using a Cameca IMS 4f equipment were performed onto the samples in order to measure the depth distribution of P, B, N, H atoms into the diamond films, with $Cs^+$ primary ions accelerated at 10 keV. In most of the samples, a single SIMS crater of approximately 150 × 150 $\mu m^2$ was dug at sample edges. The concentrations of P and B were quantified by using implanted standards. As shown in our previous papers, the phosphorus concentration of our epilayers is quite homogeneous both in depth and laterally [19]. Nevertheless, for each sample, we present the mean value of the SIMS profile on the whole layer thickness. The hydrogen and nitrogen concentrations are at the SIMS level detection limit while the residual boron concentration (contamination) is in the range 1.5–6 × $10^{16}$ $cm^{-3}$, well below the P concentration. The P concentration ranged from 3.7 × $10^{16}$ at.$cm^{-3}$ to 3.5 × $10^{18}$ at.$cm^{-3}$ and the thickness of the epilayers ranged from 1 to 6.3 µm. The relative uncertainties are estimated at 10% both for the P concentration and the film thickness.

The DC electrical measurements were performed by resistivity and Hall effect in a van der Pauw configuration from 300 K to 900 K under a DC magnetic field of 0.8 T, with a high impedance setup. The Hall scattering factor is assumed to be equal to 1. Prior to the electrical measurements, the as-grown diamond film surfaces were oxidized in order to remove the surface conductive layer due to the hydrogen termination (see Ref. [18] for details). Capacitance - voltage measurements were performed on the (100) oriented sample to determine the neutral donor concentration profile $N_D$-$N_A$ in the first 500 nm of the film (see Ref. [11] for details), with a relative uncertainty estimated at 10%.

Infrared transmission spectra were recorded from 1800 to 8500 $cm^{-1}$ in a BOMEM DA8 Fourier Transform Infra-Red (FTIR) interferometer. Liquid nitrogen or liquid helium were used to cool down the samples at temperatures ranging from 10 K to 250 K. A globar light source and a InSb detector were used. The spectral resolution was set to 4 $cm^{-1}$. The transmission was normalized to $T/T_0 = 1$ at 4000 $cm^{-1}$ where the absorption of neutral phosphorus vanishes (T: sample transmission and $T_0$: sample transmission at 4000 $cm^{-1}$). The absorption coefficient was then found from the usual relationship: $\alpha = -\frac{1}{d}\ \ln\left(\frac{T}{T_0}\right)$, d being the film thickness obtained from SIMS analysis.

## 3. Results and discussion

### 3.1. Compensation ratio and neutral donor concentration

As a result of the almost complete substitutional incorporation of phosphorus in (111) epilayers [21] and also in the (100) epilayer we have investigated [20], we consider that all phosphorus atoms incorporated in diamond in the series of samples act as donors. In other words, phosphorus are located in substitution of carbon atoms and are not complexed with other impurity or defects (ex: H or V). Consequently, we will assume that the phosphorus concentration deduced from SIMS experiments equals the concentration of donors ($N_D$).

From Hall effect measurements as a function of temperature, we deduce the compensation ratio $k = N_A/N_D$ for the (111) oriented samples by using the procedure described in Ref. [22]. The equivalent density of states effective mass was updated to $m_c^*$=1.639$m_0$ following the work of Naka et al. [23]. It follows a slightly different value of k comparing to those found in Ref. [22]. The relative uncertainty is estimated at Δk/k = 20%. For the (100) oriented sample D169b, the compensation ratio was determined by combining: (i) the neutral donor concentration $N_D$-$N_A$ extracted from C(V) measurements on the first 500 nm of the film[1] and (ii) the donor concentration $N_D$ measured by SIMS on the same part of the film. We then assumed that k is constant in the entire thickness of the film. The sample characteristics are summarized in Table 1.[2]

Let us discuss the origin of compensation in our n-type diamond layers. Residual boron acceptors are naturally compensating centers.

[1] The achievement of ohmic contact is an issue in n-type diamond. At low doping, metallic layers usually give rectifying-contact characteristics which impede Hall measurements. That's the reason why C(V) was used instead of Hall for the D169b sample which has the lowest doping.

[2] In the case of D169b which is a relatively thick layer, the phosphorus concentration slightly varies along the layer (SIMS profile can be found in Ref. [20]). The concentration given in Ref. [20,11] are averaged on the first 800 nm of the layer. This is the correct method to compare the impurity concentration with surfacic measurements such as a C(V) measurement or cathodoluminescence at low voltage. As FTIR absorption occurs in the whole film thickness, it is necessary to consider in this work the mean $N_D$ concentration over the total depth of the layer as reported in Table1.

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