Optical absorption and cathodoluminescence in homoepitaxially grown CVD diamond films [1]

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Abstract

Defect-induced optical absorption in diamond layers, homoepitaxially grown by the chemical vapour deposition technique, is investigated by the use of photothermal deflection spectroscopy (PDS). The measured spectral dependence of the optical absorption coefficient for these layers is compared with the optical absorption in type IIa natural and type Ib synthetic diamond. The measured absorption spectra show the orientation-dependent nitrogen incorporation in the homoepitaxial diamond layers. The orientation-dependent nitrogen incorporation is in agreement with the cathodoluminescence data. The characteristic subgap continuum absorption is observed in both {001} and {110} oriented diamond layers.

Keywords: Optical absorption; Cathodoluminescence; Homoepitaxial films; Defects

1. Introduction

Preparation of single-crystal diamond films by chemical vapour deposition (CVD) is of great interest for electronic applications. Apart from technological problems with the fabrication of single-crystal wafer-size diamonds [1,2], reduction of the number of defects is one of the primary goals to be achieved. These defects can induce localized states in the forbidden gap of diamond and deteriorate its electrical properties. In this work we investigate the optical absorption, related to the presence of nitrogen and/or native defects, by photothermal deflection spectroscopy (PDS). The PDS technique, used previously for studying polycrystalline diamond films [3,4] was employed here because of its significantly higher sensitivity as compared with the optical transmission measurements and its lower sensitivity to elastic light scattering [5]. With this technique absorbance values down to 10^{-5} can be measured,

compared to 10^{-2} for conventional spectrophotometers [6].

The homoepitaxial diamond layers, examined in this study, were deposited by the flame deposition technique on top of type IIa natural diamond seed crystals with {001} and {110} orientations [7]. Nitrogen, incorporated in these specimens, entered the gas phase by in-diffusion from the ambient during the film growth. For comparison, type Ib high pressure-high temperature (HPHT) synthetic diamond (containing substitutional N) and type IIa natural diamond are also investigated. Finally, the subgap optical absorption of the homoepitaxial diamond films is compared with the cathodoluminescence (CL) measurements and with the previous PDS investigations on polycrystalline diamond films [3].

2. Experimental details

2.1. Investigated samples

Characteristics of the samples investigated in this work are summarized in Table 1 and their description is given below.

Table 1
Basic characteristics of the samples

Sample	Substrate	Misorientation	Layer thickness (μm)	Colour
Ib	{110}; 4 × 2 × 0.250 mm³			Yellow
IIa	{001}; 2 × 2 × 0.250 mm³	Within 3°		White transparent
C7	{001}; ⌀ 4 × 0.51 mm³	Within 3°	370.00	Light brown, less transparent
D2	{110}; ⌀ 3 × 0.31 mm³	Within 3°	153.00	Brown opaque

2.1.1. Natural and HPHT-synthetic diamond

Diamond which contains virtually no (optically active) impurities is generally classified as type IIa [8]. Therefore type IIa natural diamond was selected as a reference sample for calibration of our PDS set-up. Type IIa diamond plates were also used as substrates for growing the homoepitaxial films.

Diamond containing single substitutional nitrogen is classified as type Ib [8]. It shows a characteristic IR absorption band at 1130 cm⁻¹ [9] and several UV–Vis absorption bands [10,11] (see Section 3). Type Ib HPHT-synthetic diamond (De Beers) was used to compare this characteristic UV–Vis optical absorption with the one measured for the CVD films. The Ib HPHT diamond plate, investigated here, shows a growth sector dependent concentration of substitutional nitrogen, which is typical for synthetic diamond [12]. The nitrogen concentration ranges from 50 to 150 ppm, as determined by IR absorption spectroscopy and using the conversion factor of Woods et al. [9].

2.1.2. Flame grown diamond layers

150 – 400 μm thick diamond layers were grown on {001} and {110} oriented type-IIa natural diamond seed crystals, using an acetylene-oxygen combustion flame. The acetylene supersaturation was between 3.9% and 5.4% and the substrate temperature was about 1200°C. In order to control the substrate temperature, the seed crystals were soldered onto a water cooled substrate holder. After the deposition, the back sides of the specimens were polished to remove both small residues of the solder and etch-pits, caused by a reaction of the solder with the diamond seed crystal. The experimental arrangement used for diamond growth is described in Ref.[13]. In the previous study [7] the specimens were examined in detail by scanning electron microscopy (SEM), Raman and IR transmission spectroscopies. It was demonstrated that the spectroscopic characteristics and the surface morphology of the deposited diamond layers are determined by the crystallographic orientation of the substrates rather than by the small differences in growth conditions [7].

In summary, the {001} layers can be generally classified as type IIa and they have a fairly smooth surface covered by macrosteps due to step bunching as well as by a limited number of square growth-hillocks. However, most of the {110} layers contain bonded hydrogen, which concentration can be determined from the IR C–H stretching bands of sp³ hybridized CH₂ groups between 2800 and 3000 cm⁻¹ (the amount of incorporated H was estimated to be 1200 ppm in the investigated sample). The {110} layers have a rough appearance due to the development of microfacets on the surface. In the present study two characteristic samples were selected from the set described above, a 370 μm thick {001} oriented sample (C7), and a 153 μm thick {110} oriented specimen (D2). Scanning electron micrographs, revealing the surface morphology of these samples, are shown in Fig. 1.

2.2. Optical absorption

The PDS set-up was used in the same configuration as in our previous work [3]. From the measured PDS signal, the optical absorption coefficient α is calculated, using the procedure described in Refs. [3–6]. Additionally, we performed transmission and reflection measurements using a Perkin–Elmer Spectrophotometer, equipped with a light-integrating sphere to determine light scattering losses. For the polished IIa and Ib diamond plates the scattering losses were negligible. These losses were also very low for the homoepitaxial {001} diamond film C7. For the {110} oriented sample D2 with microfacets developed on the surface, the transmission data were corrected for the light scattering losses.

The CL measurements were obtained using a 8200 MK II system for CL topography, equipped with a single monochromator system [7].

3. Experimental results and discussion

3.1. Optical absorption in natural type IIa and HPHT-synthetic diamond

Fig. 2 shows a plot of the energy dependence of the optical absorption coefficient α, measured for the type Ib HPHT-synthetic diamond and type IIa natural diamond plates. In case of type IIa diamond, the detected signal is just above the detection limit of our PDS set-up (only the spectral region between 1 and 3 eV was investigated by PDS for this sample).
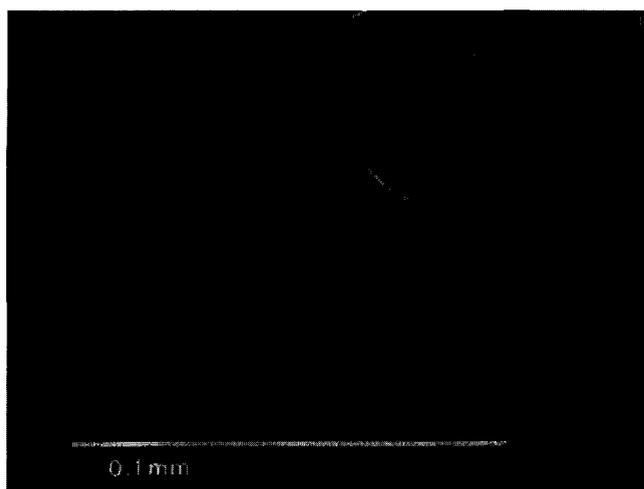
(a)
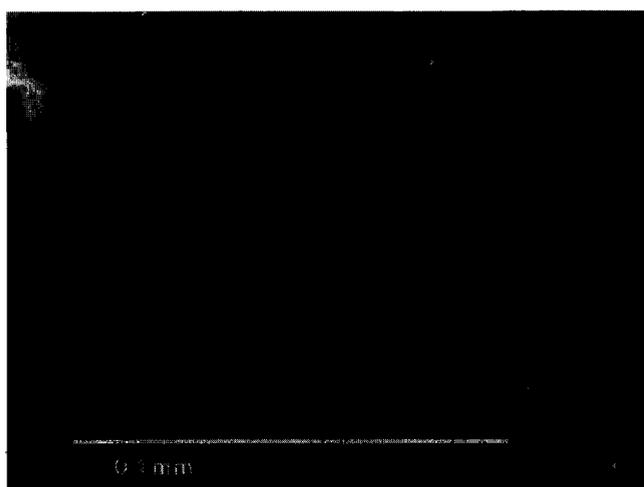
(b)

Fig. 1. Scanning electron micrographs showing the surface morphology of the homoepitaxial diamond films, deposited by the acetylene-oxygen flame technique: sample C7 deposited on a {001} oriented substrate (a), sample D2 deposited on a {110} oriented substrate (b).

Fig. 2. Spectral dependence of the optical absorption coefficient α of type Ib and IIa diamond samples, determined from photothermal deflection spectroscopy (PDS) and from optical transmission measurement.

In the case of type Ib diamond, the observed absorption is higher. At an onset of about 2.2 eV the optical absorption coefficient α, starts to rise. At higher energies, two broad bands centred about 3.3 and 4.5 eV are present. At 5.5 eV the fundamental absorption edge of diamond is observed. This spectrum agrees well with the known spectral dependence of the optical absorption coefficient α for type Ib diamond, which is due to the presence of single substitutional N [10,11].

The onset of the optical absorption at 2.2 eV was ascribed to the photoionization of the substitutional N centre [9]. Superimposed on the photoionization continuum three bands, known as the A (3.3 eV), B (3.9 eV) and C (4.5 eV) bands, were described in the Refs. [10,11]. The A and B features are overlapping and for the measurements at room temperature they are difficult to resolve. These features are probably caused by trans-
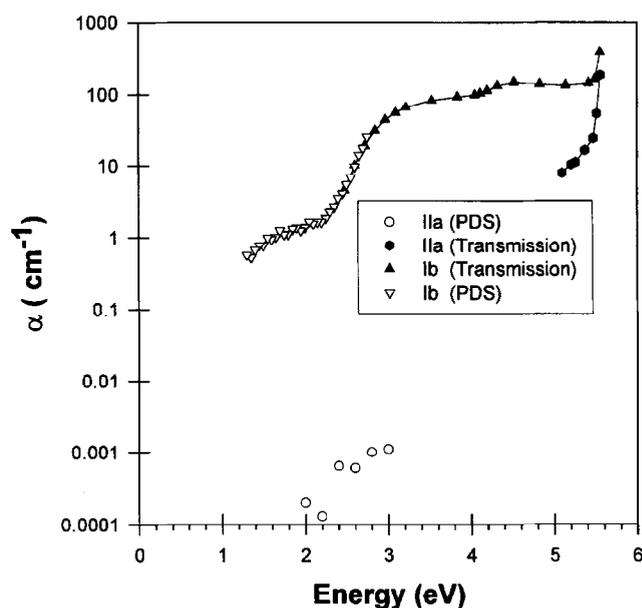
itions from the ground state to excited levels of the nitrogen centre [10]. The C band is currently attributed to a vibronic transition [14]. Low temperature measurements would be necessary to resolve the fine structure.

From the value of the optical absorption coefficient at 4.5 eV the concentration of single substitutional nitrogen was estimated to be about 90 ± 30 ppm using the conversion factor of Woods et al. [9] and the relation between the UV (4.5 eV) and IR (1130 cm^{-1}) absorption bands from work of Nazaré et al. [11]. This value is obtained by integration over a sample area of 1×2 mm^2. This is in good agreement with the IR measurements using a focused light beam, where values in the range 50–150 ppm were found for different locations at the sample.

A broad feature is observed in the low energy part of the absorption spectrum of type Ib diamond. A similar spectral dependence of α was observed for polycrystalline CVD films [4], where it was ascribed to π–π^* transitions in CVD films. To our knowledge the presence of π-bonded carbon in Ib diamond was not reported before. The observed absorption feature seems more likely to be caused by the presence of Ni in Ib-HPHT diamond [14].

3.2. N-related absorption in homoepitaxial diamond layers

Fig. 3. shows the spectral dependence of the optical absorption coefficient α for the flame grown single-crystal diamond layers, compared to the optical
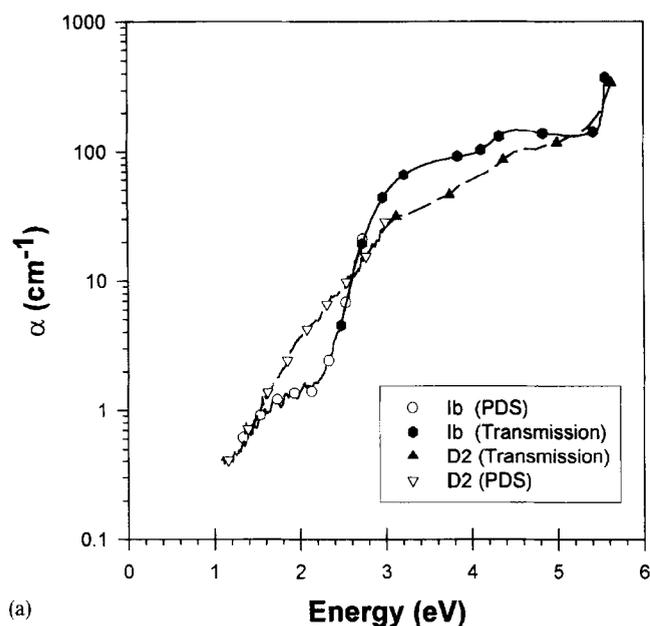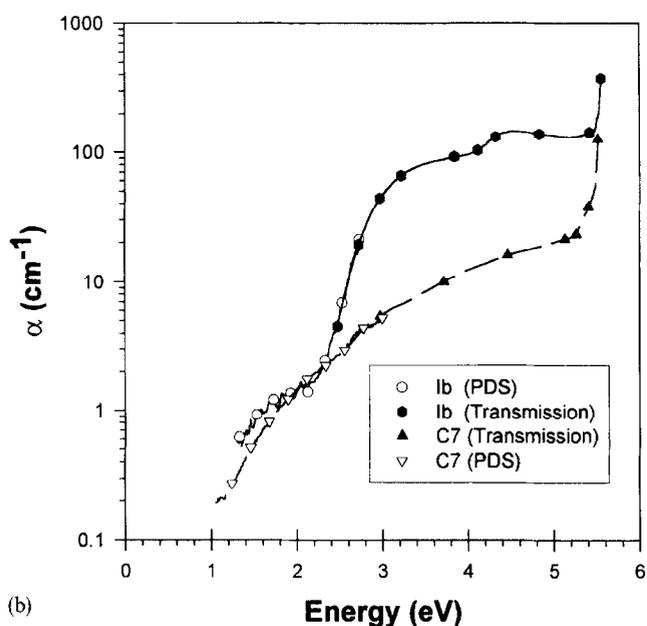
Fig. 3. Spectral dependence of the optical absorption coefficient α of the samples D2 (a), and C7 (b) compared with Ib diamond sample. The symbols in the plots correspond only to a fraction of the measured data points.

absorption coefficient for the type Ib diamond plate. The {001} sample C7 shows a continuously increasing subgap absorption, starting at the onset of the measurement at 1 eV and rising up to the fundamental absorption edge. This feature is discussed in Section 3.3.

The {110} oriented diamond film D2 also shows the characteristic continuum absorption in the low-energy part of the absorption spectrum. Starting at an onset of 2.2 eV broad features centred at about 3.3 eV and 4.5 eV are superimposed on this continuum absorption. The

shape of the optical absorption coefficient in this spectral region is identical with the one measured for type Ib diamond. After subtraction of the characteristic subgap absorption, using a fitting procedure described in Ref. [4], an optical absorption coefficient of about 30 cm^{-1} at 4.5 eV is obtained. Using the conversion factors from Refs. [9,11], this corresponds to a N concentration of about 15 ppm. To our knowledge, this is the first confirmation of substitutional N in CVD diamond obtained from ultraviolet optical absorption measurements. Recently, McNamara et al. [15] demonstrated by IR absorption measurements, that single substitutional N can be present in CVD diamond films. In Ref. [13] no N was found by IR spectroscopy in either sample D2 or C7. It should be noted that a concentration of 15 ppm N would correspond to an absorption coefficient value of about 0.7 cm^{-1} at 1130 cm^{-1} (absorbance value of 1×10^{-2}). For the diamond layer D2, which shows considerable light scattering in the IR part of the spectra, this value is very close to the IR-spectrophotometer detection limit.

The observed differences in nitrogen incorporation in the homoepitaxial films grown on {001} and {110} oriented substrates are in agreement with the cathodoluminescence (CL) results [7], shown in Fig. 4. The CL spectrum of the top face of the {110} oriented film D2 revealed the well-known orange-red CL system with a zero phonon line (ZPL) at 2.145 eV, due to the presence of nitrogen-vacancy (N-V) pairs.

However, the top face of sample C7 showed a CL spectrum, dominated by blue band A luminescence which is characteristic for type IIa natural diamond. In addition, a relatively small signal of the 2.145 eV system was observed for this sample. CL topography revealed that this orange-red system originates from an area with rough, partly curved step bunch patterns. Thus both,
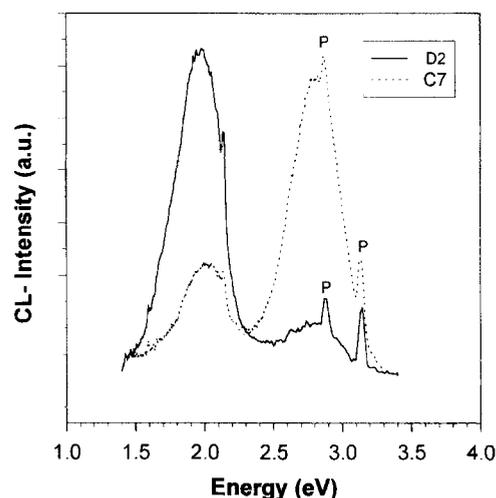

Fig. 4. Cathodoluminescence (CL) spectra of the top surfaces of the flame grown homoepitaxial diamond layers D2 and C7. The plasma peaks produced in the CL unit are denoted by P.

the PDS and CL techniques present clear evidence for the incorporation of nitrogen — albeit in different forms — only in the {110} grown film.

The orientation dependent nitrogen incorporation is most readily explained by a difference in the growth mechanism, which depends on the orientation of the seed crystals. The {001} oriented films grow by a layer mechanism via the incorporation of growth units at steps [16]. In this way the uptake of impurities (e.g. hydrogen or nitrogen) is generally quite low. The {110} surface is fully stepped (see Fig. 1b) and impurities are relatively easily trapped in the growing diamond film. The local incorporation of nitrogen in the area with rough step bunch patterns on the {001} oriented specimen, as observed by CL-topography [7], is in full agreement with this explanation. In contrast with the smooth macrosteps on the {001} aligned along the in-plane ⟨110⟩ directions (see Fig. 1(a)), the rough macrostep bunches are curved. Therefore, these macrosteps have a high density of kink sites and the incorporation of impurities becomes more likely than for the smooth step bunches [17].

3.3. Continuum absorption in homoepitaxial diamond layers

The characteristic continuum absorption has been observed by PDS for the polycrystalline diamond samples, grown by the microwave plasman-enhanced CVD technique [4]. This feature was ascribed to π–π^* transitions in amorphous carbon regions present in polycrystalline films on grain boundaries. A similar conclusion concerning the presence of the amorphous carbon in grain boundaries was suggested in Ref. [18].

In homoepitaxial diamond layers, the characteristic continuum absorption was expected to be significantly reduced. However, π-bonded carbon can readily occur at the surface of a crystal due to surface relaxations and reconstructions or even due to surface absorbates. Here, the surface roughness caused by step bunching on the surface of the {001} oriented layer and due to microfacets on the {100} oriented diamond layer might enhance these effects significantly. It is interesting to note that in the literature π-bonded carbon clusters were also suggested as an explanation of the radiation damage-induced optical absorption in IIa diamond [19]. A detailed PDS investigation of homoepitaxially grown CVD diamond is currently being carried out.

4. Conclusions

In summary, the spectral dependence of the optical absorption coefficients in homoepitaxial diamond films grown by the flame technique were investigated and compared to the spectra of type Ib and IIa diamond.

The diamond films deposited on {110} oriented substrates exhibit a similar spectral behaviour of the optical absorption as type Ib diamond. Using the conversion factors from Refs. [9,11] we estimate N concentrations to be around 15 ppm in this sample. For layers deposited on {001} oriented substrates, no N-related absorption could be detected. The results on the orientation-dependent nitrogen incorporation are in good agreement with the cathodoluminescence data.

All CVD grown samples exhibit a characteristic continuum subgap absorption, which was absent in type IIa diamond. The continuum absorption is very similar to that observed for high quality polycrystalline diamond films, where it was attributed to π–π^* transition due to the presence of amorphous carbon (a-C) [4]. In the investigated homoepitaxial diamond single crystals, step bunches on the {001} oriented layer and microfacets on the {110} oriented layer might provide sites for an a-C phase at the surface. More detailed investigations of the continuum absorption in single crystals CVD diamond will be the subject of a future study.

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