Transient photoconductivity spectroscopy of polycrystalline diamond films

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Abstract. Photoexcitation spectra of nonequilibrium charge carriers in polycrystalline diamond films were measured in the visible region (430 – 690 nm) by the contact-less transient photoconductivity technique with a tunable optical parametric oscillator. Preliminary irradiation of samples by intense UV laser pulses resulted in the redistribution of the population of deep trap levels and was accompanied by substantial long-term enhancement of photoconductivity in the spectral band at 2 eV.

1. Introduction

A unique combination of the properties of polycrystalline diamond films and the substantial progress achieved in the tech-nology of their growth make these materials attractive for applications in optics and laser technology [1] as well as in modern electronics. At present, polycrystalline diamond films are very similar in their properties to the purest natural diamonds. These films are characterised by a broad band gap, high optical damage resistance, high mobility and short recombination times of free electrons and holes, and very high thermal conductivity [2].

However, the band structure of both natural and synthetic diamonds is significantly complicated by the diversity of intrinsic and impurity defects whose energy levels are located in the band gap [3]. For this reason properties of diamonds are determined primarily by the processes of population and relaxation of deep electron centres, which can result in the dependence of these properties on the previous treatments of the sample irradiation.

Conventional photoconductivity measurements at room temperature [4] showed that the photosensitivity of polycrys-talline diamond films increased in a wide spectral range after irradiation by UV light in the region of the interband transi-tions. The induced photoconductivity spectrum was diffuse and exhibited no details. Therefore it was not possible to identify the electronic transitions responsible for photosensi-tisation. The diffuseness of the spectrum can be due to the stationary mode of photoconductivity measurements and the stepwise relaxation of nonequilibrium electrons through

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a series of intermediate levels. The characteristic exposure time of the tunable probe radiation in the experiments [4] was significantly longer than both the lifetime of free elec-trons and the time of their retention by intermediate electron centres. In this case, the photoexcitation (including cascade transitions) and stepwise relaxation of conduction electrons induce a quasi-equilibrium population distribution in the crystal band gap. Consequently, the contribution of intermediate levels to the measured photoconductivity increases significantly.

The localisation of relatively shallow populated traps in diamond films exposed to UV radiation was also evaluated by measuring thermostimulated conductivity [5]. Unfortu-nately, material properties cannot be examined in situ by this technique, and the data obtained cannot be interpreted without making assumptions about the mechanisms of recombination and population of the defect levels.

2. Method of spectral measurements

In this work, the structure of diamond impurity levels was, for the first time, studied by the spectroscopic method com-bining the use of a tunable source of short (~ 1 ns) laser pulses with the detection of free charge carriers by the tran-sient photoconductivity (TPC) technique. This method was originally proposed for studying multiphoton absorption in wide-gap optical crystals [6 – 8]. More recently it was adapted to study impurity absorption in materials with high-mobility free charge carriers [9, 10].

Fig. 1 shows the scheme of measurements. The TPC tech-nique avoids the serious problem of creating ohmic contacts, and implies that a current pulse is measured by an electric circuit containing a photoconducting capacitor cell (1) with the sample (2) placed inside it. The current pulse is induced by a rapid displacement of free charge carriers in the part of the sample irradiated by the laser (away from the sample boundaries) upon application of a high-voltage (3.6 kV) pulse across the cell electrodes. To avoid polarisation of the sample due to the dark current flowing in the interval between laser pulses, the external electric field is applied for only a short time interval (~ 20 μs) that includes the instant of irradiation.

The samples (2) were polycrystalline diamond films 10 mm $\times$ 8 mm $\times$ 0.35 mm in size. The films were synthes-ised by chemical vapour deposition, separated from the silicon substrate, and mechanically polished. A sharp peak of width 2.5 cm^{-1} observed in the Raman spectrum at 1332 cm^{-1} indicated that the diamond plate was of high struc-tural quality and did not contain a significant amount of nondiamond carbon phases [11]. The concentration of the substitutional nitrogen impurity atoms deduced from the
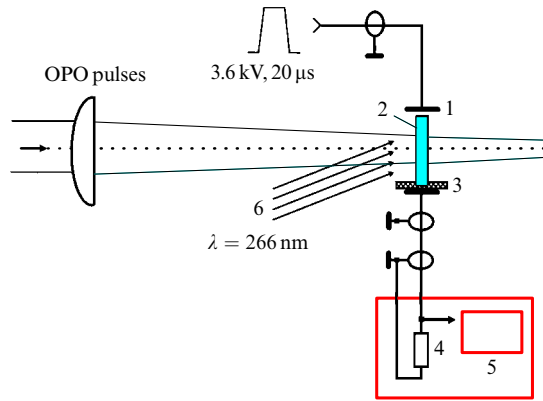
Figure 1. Scheme of measurements of the UV sensitisation spectra in a diamond film by the TPC technique: (1) measuring capacitor, (2) sample, (3) Teflon sample holder, (4) 50 Ω load resistor, (5) pulse oscilloscope, (6) sensitising UV radiation.

270 nm absorption band was 3×10^{17} cm^{-3} [12]. We used an optical parametric oscillator as the source of radiation tunable in the visible spectral region from 430 to 690 nm and generating laser pulses of duration 1.5 ns. The TPC spectra were obtained by measuring the dependence of the induced photocurrent [or the voltage pulse across load resistor (4) of pulse oscilloscope (5) series connected in a circuit with photoconducting cell (1)] on the energy of the exciting radiation. The data set obtained for various wavelengths was subsequently normalised to an energy of 50 μJ.

Fig. 2 displays one of the experimental dependences obtained at the emission wavelength 460 nm. We found that the photoresponse was close to linear throughout the entire spectral tuning range, similar to the dependence presented in Fig. 2. Because the measured signal amplitude U_{pc} is proportional to the number of nonequilibrium charge carriers N induced in the conduction band [7], the linear dependence observed experimentally indicates that single-quantum transitions to the conduction band from energy levels located in the crystal band gap and associated with various impurity and
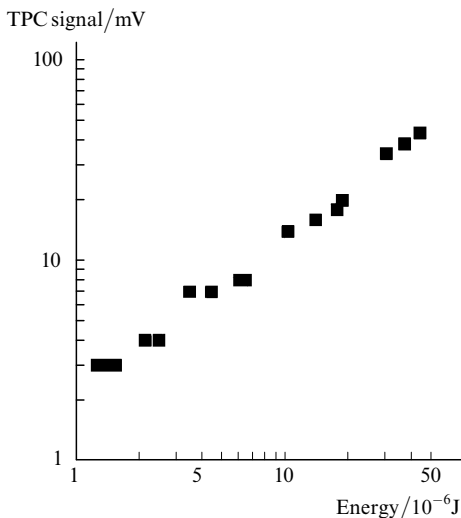
intrinsic electron centres play a dominant role. Using the basic relationships for the transient photoconductivity signal measured in the case of single-photon absorption [7, 10] and taking into account that the linear recombination time τ_r determined previously for the given sample ($\tau_r \approx 2$ ns) [13] is comparable with the duration τ of the laser pulse, one may write

$$U_{pc} = \alpha \frac{\mu e E_0}{\varepsilon L^2 R} N . \tag{1}$$

Here, e and μ are the electron charge and mobility, E_0 is the applied voltage, L and $R = 50$ Ω are the distance between the measuring capacitor plates and the load resistance, $\varepsilon = 5.7$ is the dielectric constant of diamond, and $\alpha \approx 1$ is a geometric factor taking into account the deviation of the field distribution inside the photoconducting cell from a homogeneous distribution induced by an ideal flat capacitor. With regard to the parameters listed above and the focusing geometry, we can estimate the concentration of nonequilibrium charges as follows:

$$n = k U_{pc} , \tag{2}$$

where the proportionality factor $k \approx (2.2 - 4.5) \times 10^{13}$ V^{-1} cm^{-3}. The uncertainty in the factor k is due to the uncertainty in the measured mobility μ of free electrons in the range $500 - 1000$ cm^2 V^{-1} s^{-1} [10].

One can see that this method is highly sensitive and that the lowest electron concentration detectable experimentally is 5×10^{10} cm^{-3}. It should be noted that the simple expressions (1) and (2) used here are valid only under the assumption that the screening of the electric field of the measuring capacitor due to the space charge separation in the illuminated area is negligible. This is true when $\tau_r < \tau_s$, where $\tau_s = \varepsilon \varepsilon_0 / ne\mu$ is the screening time, and ε_0 is the permittivity of vacuum. In our measurements, this condition is fulfilled satisfactorily up to concentrations of $n \approx 10^{12}$ cm^{-3} of nonequilibrium charge carriers.

3. Experimental results and conclusions

The measurements were performed at room temperature on the same sample of polycrystalline diamond taken in the initial state, after its irradiation with a series of several UV laser pulses (266 nm, 250 MW cm^{-2}), and after annealing of the sample in air at a temperature of 450 °C. The spectral dependences are shown in Fig. 3, where the transient photoconductivity signal, normalised as indicated above, is plotted on the vertical axis. The size of points in Fig. 3 corresponds approximately to the experimental data spread. The long-wavelength part of the initial spectrum exhibits features that were absent both in the transmission spectrum measured previously and in the stationary photoconductivity spectrum [4].

After intense UV irradiation of the crystal, the transient photoconductivity signal increased significantly throughout the entire visible range. The highest rise (by more than an order of magnitude) was observed in a relatively narrow spectral band at 2 eV. It was found that the photosensitisation is characterised by a long lifetime. At room temperature (20 °C) it disappeared completely after two days. A drop in the transient photoconductivity signal was also observed after prolonged exposure to multipulse visible radiation from an optical parametric oscillator. To avoid possible bleaching of the induced photoconductivity during measurement of
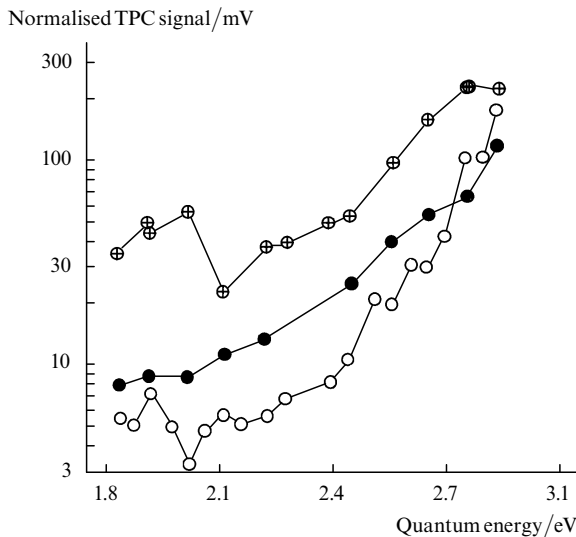

Figure 2. Dependence of the TPC signal on the laser energy measured in a polycrystalline diamond film at a wavelength of 460 nm.

Normalised TPC signal/mV

Figure 3. TPC spectra of a polycrystalline diamond film: initial (○), after irradiation with a series of UV laser pulses (266 nm, 250 MW cm^{-2}) (⊕), and after annealing in air at 450 °C (●).

the spectrum, the sample under study was additionally exposed to a fixed dose of UV laser radiation before each series of measurements. After being annealed in air for a short time, the induced photoconductivity peak disappeared, and the average photoconductivity decreased.

The mechanism of induced photoconductivity and the parameters of the electron centres involved can be determined from the data obtained. Thus, although the energy 4.66 eV of the UV quantum that causes sensitisation is lower than that of the interband transitions in diamond, the UV quanta efficiently generate nonequilibrium electrons in the conduction band, whose concentration amounts to 10^{16}–10^{18} cm^{-3} at an irradiation intensity of 250 MW cm^{-2} [10]. In these circumstances, electrons can be provided by defects, which represent substitutional nitrogen impurity atoms and contribute to the electronic component of photoconductivity at an energy of the exciting quantum close to 4 eV [14]. The nonequilibrium charge carriers are then captured by deep traps lying 1.9–2.0 eV below the bottom of the conduction band and are held there for a long time. It is the population of the trap levels, which increased by a large factor, that enhances the photosensitivity of the material in the visible spectral region. The process of capturing charge carriers by using deep traps evidently involves intermediate steps with the participation of a set of more shallow levels. It occurs in a period of time that exceeds both the time τ_r and the duration τ of the exciting laser pulse, which apparently explains distinctions between the conventional [4] and transient photoconductivity spectra. Defects representing interstitial carbon atoms or impurities can serve as the centres of final trapping [14].

We have demonstrated by the example of a synthetic polycrystalline diamond that the TPC technique is advantageous for studying the photoconductivity in wide-gap dielectrics and semiconductors. Under intense irradiation of the material at a wavelength that does not induce interband transitions, the population of deep trap levels increased more than ten times. The level depth was determined by a direct method at room temperature, i.e., under conditions of interest primarily for practical applications.

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