Influence of air annealing on the luminescence dynamics of HPHT nanodiamonds

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A R T I C L E   I N F O

A B S T R A C T

We present a study of the influence of air-annealing on the photoexcited charge carriers dynamics on the surface of nanodiamonds of sub-10 nm size. Samples were produced by high temperature annealing of high-pressure, high-temperature nanodiamonds. Measured photoluminescence spectra of annealed nanodiamonds show distinct blue shift and spectral narrowing compared to non-annealed reference. Time-resolved measurements revealed a change in relaxation process in the nanodiamond surface layer due to removal of non-diamond carbon phase on the surface. Spectro-temporal evolution takes place during the first 50 ps after photoexcitation suggesting that non-radiative states play a major role in the charge carrier relaxation. The acceleration of high energy states depopulation, observed for the annealed nanodiamonds, suggests gradual inhibition of non-radiative recombination channels (originally present in large numbers in non-annealed sample), which is in a good agreement with the picture of reduction of non-diamond carbon phase.

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1. Introduction

Diamond nanoparticles (i.e. nanodiamond, ND) represent a promising nanomaterial for a broad spectrum of application. Nanodiamond inherits most of the bulk diamond exceptional physical properties such as hardness, non-toxicity and bio-compatibility [1], which makes it useful for protective surface coating, biological sensing or drug delivery in biological systems [2–5]. By introducing nitrogen, silicon and other suitable atoms in the diamond lattice one can obtain stable single photon sources [6] usable in fluorescent imaging, quantum computing [7] or nanoscale sensor of a single electron spin [8]. For all these applications the properties of the surface of diamond nanocrystals and surface related carrier energy states represent crucial factors connected with their chemistry [9], opto-electronic processes [10], and photoluminescence [11]. On the other hand, the presence of a high number of nanocrystal surface states affects strongly also the optical response of material as light absorption and photoluminescence. The smallest nanodiamonds that have been prepared artificially so far are too large in comparison with the exciton Bohr radius of 1.6 nm to influence the core electronic states so that their electronic states correspond well to the bulk diamond bands [11]. The engineering of the nanodiamond size and surface will open prospects for studies and applications of size confinement effects in diamond [12–14].

Typical ways of ND production for industrial and research purposes are either synthesis by the detonation technique or mechanical milling of high-pressure, high-temperature (HPHT) diamond microcrystals. Formation of detonation nanodiamonds [15] is specific because of its narrow size distribution of about 5 ± 2 nm. Structure of such particles consists mainly of diamond core with possible lattice defects and graphitic surface layer to which diverse functional groups may be attached. On the other hand, NDs formed by milling of HPHT diamond powder of median size of 18 nm are proposed to contain minimum lattice defects and should have rather uniform structure [16]. Grinding process with consecutive centrifugation [17] are techniques for obtaining sub-10 nm NDs. In addition, Stehlik et al. [16] successfully achieved great purity and crystallinity by annealing NDs in air followed by centrifugation thus obtaining nanodiamonds of excellent quality and with size distribution similar to detonation nanodiamonds. In such ~3 nm monolithic HPHT NDs, phonon confinement effects were already observed by Raman micro-spectroscopy.

In this paper we study the dynamics of charge carriers in sub-band gap states (i.e. states related predominantly to the nanocrystal surface) of these ~3 nm HPHT NDs by means of ultrafast photoluminescence spectroscopy. Ultrafast time-resolved spectroscopy provides direct information on initial photoexcited carrier relaxation and recombination and is therefore unique tool for investigation of photoluminescence (PL) mechanism in nanodiamond, which is still – despite some previous research [18] – not well understood. We used a streak camera to investigate spectro-temporal evolution of PL spectra on the picosecond time

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scale. We concentrate on the effect of thermal annealing on opto-electronic properties of NDs.

2. Material and methods

Samples studied in this paper were prepared from MSY0-05 nanodiamond powder (Microdiamant AG, Switzerland) with mean size of 18 nm. This powder was used as received (ND-AR), annealed at 450 °C for 30 min (ND-450), and annealed at 500 °C for 30 min (ND-500) for further preparation of colloidal solutions. Additionally, sample ND-700-H made by annealing of ND-450 at 700 °C for 3 h in hydrogen atmosphere was used to confirm direct effect of the heat treatment on the ND surface. Colloidal solutions were prepared from 4 mg of related ND powder and 1 ml of de-ionized water. Homogenization was performed by 1 h sonication using ultrasonic horn at 200 W (Hielscher). Then 1 ml of de-ionized water was added and the solution was centrifuged for 1 h at 14,000 rpm (13,124 × g) (Eppendorf Mini plus). Finally, 1 ml of supernatant was carefully extracted by a micropipette. Interesting feature of such prepared samples is the size distribution which is very similar to that of detonation nanodiamonds. Note also that annealing at 450 °C suppresses surface graphitic phase and, therefore, leads to a higher purity of the system from the perspective of sp^3 diamond phase. Annealing at 500 °C leads also to oxidative diamond etching and thus to further reduction of nanodiamonds size and non-diamond phase content [16]. For optical measurements, the colloidal solution was dropped on top of fused silica substrate and slowly dried under ambient atmosphere and temperature.

Standard PL was excited by 325 nm line of continuous wave He—Cd laser with intensity 800 W/cm^2 and measured by a CCD camera (Andor iDus) attached to grating spectrograph. The data were corrected for the spectral response of the whole set-up.

For the time-resolved PL measurements, we used excitation by 360 nm femtosecond pulses obtained by frequency doubling of the fundamental laser output of a Ti:sapphire femtosecond laser (Newport/Spectra Physics). The pulse parameters were 70 fs time duration, 80 MHz repetition rate, and peak power density 2.3 kW/cm^2 on the sample. The PL dynamic was measured by a streak camera (Hamamatsu, Fig. 1) in synchroscan regime; various time ranges were used. The streak camera was coupled to the spectrograph to obtain information on spectro-temporal evolution of the PL signal in a wide spectral interval of 400 nm–800 nm.

3. Results and discussion

Normalized PL spectra of studied samples are shown in Fig. 2. PL was excited by 325 nm continuous-wave laser line which means that the carrier sub-gap states are directly populated by light absorption. PL band of ND-AR (black curve) sample is very broad covering the whole visible spectral region with a maximum around 500 nm. There is a slight difference in the spectral maximum positions of samples ND-AR and ND-450 (red curve). Moreover, spectral narrowing is observable for 450 °C annealed sample. On the other hand PL maximum of sample ND-500 (blue curve) is distinctly shifted towards the blue spectral region with 430 nm maximum. In addition, the PL spectrum of sample
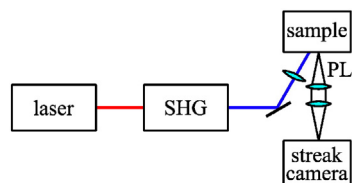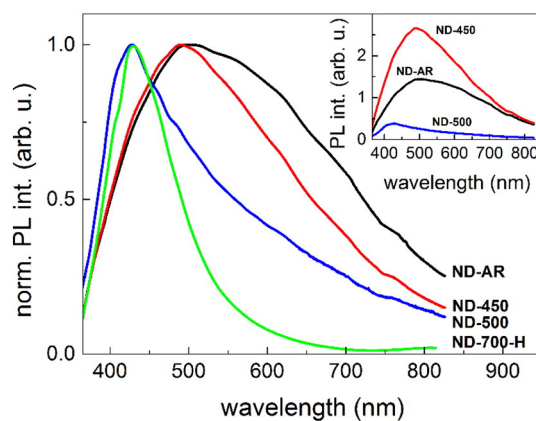

Fig. 2. Normalized photoluminescence spectra of ND samples (cw excitation at 325 nm). Inset: PL spectra before normalization (PL spectrum of sample ND-700-H is not shown due to its different concentration). (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

ND-700-H, which underwent hydrogen passivation, is shown (green curve). It has the narrower PL band with the same peak wavelength as sample ND-500. Similar influence of annealing on PL spectra of nanodiamond samples including the blue shift of the PL maximum was reported previously by Stehlik et al. [16].

In order to compare the PL intensity of samples with the same nominal concentration of ND particles in deionized water, we show the non-normalized PL spectra in the inset of Fig. 2. The signal of ND-450 sample is larger, the signal of sample ND-500 is weaker. We do not include sample ND-700-H because of its unknown concentration. The PL intensity scaling can be connected with changes in the absorption coefficient at the excitation wavelength or by modification of photoluminescence efficiency. Measured comparable values of absorption coefficient of all three samples suggest that different PL intensity is caused by different PL efficiency due to modification of carrier non-radiative recombination channels by annealing.

In this paper we concentrate on the carrier dynamics immediately after photoexcitation, i.e. on the PL decay on a time scale of picoseconds. Results of the streak-camera measurements can be presented as dynamics of PL in particular spectral interval (at selected wavelength) or as a spectrum of PL at given time (after excitation). In Fig. 3, the PL dynamics in the spectral interval of 20 nm around central wavelength of 500 nm for samples ND-AR and ND-450 is shown in a semi-log plot.

Significant differences in the PL dynamics of the two samples are clearly apparent. The standard PL spectra of samples ND-AR and ND-450 are very similar but the PL decays at the peak wavelength (about 500 nm) differ – see Fig. 3. The decay of the ND-450 sample is much

Fig. 1. Experimental set-up for time-resolved measurements. Fundamental laser wavelength (760 nm) is transformed into 360 nm by frequency doubling (second harmonic generation). PL was focused on the entrance slit of spectrograph coupled to streak camera.
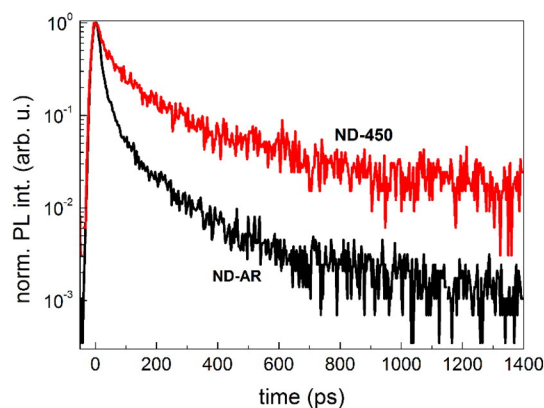

Fig. 3. Comparison of PL dynamics at 500 nm for samples ND-AR (black curve) and ND-450 (red curve) (semi-log scale). (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)