



Photoluminescent properties of single crystal diamond microneedles



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ABSTRACT

Single crystal needle-like diamonds shaped as rectangular pyramids were produced by combination of chemical vapor deposition and selective oxidation with dimensions and geometrical characteristics depending on the deposition process parameters. Photoluminescence spectra and their dependencies on wavelength of excitation radiation reveal presence of nitrogen- and silicon-vacancy color centers in the diamond crystallites. Photoluminescence spectra, intensity mapping, and fluorescence lifetime imaging microscopy indicate that silicon-vacancy centers are concentrated at the crystallites apex while nitrogen-vacancy centers are distributed over the whole crystallite. Dependence of the photoluminescence on excitation radiation intensity demonstrates saturation and allows estimation of the color centers density. The combination of structural parameters, geometry and photoluminescent characteristics are prospective for advantageous applications of these diamond crystallites in quantum information processing and optical sensing.

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1. Introduction

Optical properties of diamond are one of the most attractive characteristics of this material [1], allowing its various applications spanning from jewelry, where the refractive index and optical absorption features are the most important [2], up to quantum information processing and optical sensing, where color centers presented in diamond are exploited [3,4]. Nitrogen-vacancy center is the most commonly considered as quantum optical element [4]. At the same time high abundance of nitrogen in the environment results in technical difficulty for synthesis of diamond free of

nitrogen incorporated into its crystal structure [5]. The diamond color centers related to silicon, nickel and some other impurities, which are more suitable for controllable introduction, are also attractive for the purpose of quantum information processing [5]. Among the major challenges for quantum optics applications are also the controllable shaping of diamond-based structures and localization of the color centers. These two factors are critically important for utilization of their inherent potential [6–8]. The appropriate diamond shaping has been performed using the top-down nanofabrication technique to provide isolated color center [9]. Alternatively small size diamond crystallites (nano-diamonds) containing individual color centers can be used [10]. These types of diamond nano-structures as well as nano-diamond particles have high potential in bio-imaging and magnetic field sensing [10,11]. However practical applicability of these achievements remains

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challenging because of low reproducibility of photonic and geometrical characteristics of these nano-diamond structures. We suppose that the desired combination of nanometer sizes of the crystallites with the possibility for its controllable manipulation may be achieved with diamond structures shaped in elongated (e.g. needle-like) forms.

In this paper we describe the results of our recent investigation of photoluminescent (PL) properties of the rectangular pyramid shaped single-crystal diamond crystallites. Reproducible mass production of these diamond crystallites was demonstrated recently [12,13]. The investigation is aimed by obtaining characteristics of the diamond needles suitable for evaluation of their applicability in quantum optics. The luminescent spectral characteristics and their dependence on the excitation wavelength were studied for the powder samples of the diamond needles while the intensity distribution and time decay of the PL lines were studied for the individual crystallites. The color centers type, distribution, density and localization in the diamond needles were revealed. In combination with previously developed methods for manipulation of individual crystallites and their assembling with appropriate holders [14–17], the obtained information may be used to extend the diamond needles application to local optical and magnetic sensing and imaging.

2. Materials and methods

The CVD growth of polycrystalline diamond films was performed using home made system described in details elsewhere [12,13]. The hydrogen-methane gas mixture was activated by DC discharge ignited between two Mo electrodes of 50 mm in diameter located at a distance of 50 mm from each other. The deposition parameters were chosen in order to provide a mixture of nano-diamond material with inclusions of well developed microcrystalline diamonds: the substrate temperature was about 900 °C; gas mixture composition of $\text{CH}_4:\text{H}_2 = 5:95$; total gas pressure of 9.5 kPa; DC discharge voltage of 700 V and current density of 1 A cm^{-2} , the deposition process duration was chosen depending on desirable length of the diamond crystallites taking in account that average growth rate is about $1 \mu\text{m h}^{-1}$. The substrates for diamond films deposition were made of standard silicon wafers (Si (100), 460 μm thickness). Before being used for diamond deposition the substrates were treated by micrometer sized diamond powders to create nucleation sites. The treatments were made by ultrasonication in an aqueous suspension of the diamond powder. Substrate temperature was controlled during deposition using optical pyrometer. Variation of substrate temperature, gas composition, and discharge current was used to provide formation of diamond crystallites with different geometrical characteristics [13]. The thermal oxidation of the diamond films was performed in a furnace at 650 °C in air under a normal atmospheric pressure for 20 h. The heating in air allowed selective oxidation of the nano-sized diamond and non-diamond carbon fractions. Carbon oxides volatilization leaves only pyramidal crystallites of micrometer size. After oxidation the crystallites are easily detached from the substrate. They were collected together as a powdered material or were individually disposed on suitable surface or manipulated using appropriate techniques.

SEM analysis of obtained materials was performed using a LEO 1550 (Zeiss) microscope.

All optical measurements in this work were performed at room temperature in ambient atmosphere. The photoluminescence (PL) measurements including the excitation (PLE) spectra analysis were performed for the powdered diamond crystallites disposed on the quartz substrates. The PL and PLE spectra were recorded with Horiba Jobin-Yvon NanoLog system supplied with a

photomultiplier (R928P) with a spectral range of 180–850 nm. Xe lamp was used for PLE measurements in ultraviolet and visible ranges from 250 to 900 nm.

Also individual diamond needles were investigated by home built confocal microscope under continuous wave 532 nm laser excitation and their PL spectra were recorded [18]. Laser light was focused by an oil immersion objective with $\text{NA} = 1.35$. Fluorescence collected by the same microscope objective passed through a band-pass filter and a spatial mode filter before it was detected by a single-photon avalanche diode. In case of high photon rate the luminescence was attenuated by neutral filters. PL spectra were measured by a grating spectrograph combined with a cooled CCD camera.

Fluorescence lifetime imaging microscopy (FLIM) mapping was done using Olympus IX71 confocal microscope system equipped by Princeton Instruments piezoscanners, 485 nm ps diode laser (with 40 MHz repetition rate) and single photon avalanche diode detectors (Micro Photon Devices).

3. Results and discussion

3.1. Geometrical characteristics and photoluminescent properties of the diamond needles

With appropriate choice of the CVD parameters (methane concentration and substrate temperature) produced polycrystalline diamond films were composed of micrometer size crystallites surrounded by nano-diamonds, graphitic, and disordered carbon. The heating in air allows selective oxidation of the nano-sized diamond and non-diamond carbon fractions. Carbon oxides volatilization leaves only pyramidal crystallites of micrometer size. After oxidation the crystallites are easily detached from the substrate. They were collected together as a powdered material or individually disposed on suitable surface and manipulated using appropriate techniques.

The needle-like shape of the diamond crystallites is due to mechanisms inherent for CVD and their size and geometry are determined by the deposition process parameters [13]. The angle of the pyramids depends on gas composition and plasma activation energy, which is determined by current density of the DC discharge. If growth parameters are stabilized in time, the angle of diamond pyramids is constant along a whole crystallite (Fig. 1). The variation of the activation energy (i.e. DC discharge current) provides controllable change of the angle and shape of the crystallites [13]. The examples of the possible shape variations are shown in Fig. 1a–f. Pyramid angle and transverse size of the needles may be varied repeatedly with corresponding changes of CVD parameters (Fig. 1g). The crystallite shape is also sensitive to the gas mixture composition during the CVD [19]. The length of the diamond needles is determined by deposition process duration with the average growth rate of about $1 \mu\text{m h}^{-1}$. Independently on the length typical transverse dimension of the crystallite apices were in the range of 2–200 nm (Fig. 1a–f). The mechanisms of CVD processes determine also crystallographic orientation and surface morphology of individual particles composing the polycrystalline diamond films [12,13]. The [100] crystallographic axis is directed along the needle. The pyramid rectangular basis coincides with (100) crystal plane. The (100) basis surface has high flatness in contrast to pronounced roughness of the lateral surfaces which are formed by atomic terraces of (111) and (110) facets. At the same time sharpness of the apices, which is varied from 2 to 200 nm, depends on parameters of both CVD and selective oxidation processes. Small size fragments of other needles are appeared occasionally on the lateral surfaces due to electrostatic interaction (Fig. 1b).

It should be noted that we did not find any significant variation

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