



Full Length Article

Photo- and cathodo-luminescence of needle-like single crystal diamonds



Feruza T. Tuyakova^{a,b}, Ekaterina A. Obraztsova^{b,c,d}, Evgeny V. Korostylev^e,
Dmitry V. Klinov^{c,f}, Kirill A. Prusakov^f, Andrey A. Alekseev^g, Rinat R. Ismagilov^g,
Alexander N. Obraztsov^{a,g,*}

^a University of Eastern Finland, Department of Physics and Mathematics, Joensuu 80101, Finland

^b Moscow State Institute of Radio Engineering, Electronics and Automation, Moscow 119454, Russia

^c M.M. Shemyakin and Yu.A. Ovchinnikov Institute of Bioorganic Chemistry, Russian Academy of Sciences, Moscow 117997, Russia

^d A.M. Prokhorov General Physics Institute, Russian Academy of Sciences, Moscow 119991, Russia

^e Moscow Institute of Physics and Technology, Dolgoprudny 141700, Russia

^f Research Institute for Physico-Chemical Medicine, Moscow 119435, Russia

^g M.V. Lomonosov Moscow State University, Department of Physics, Moscow 119991, Russia

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ABSTRACT

Comparative study of photoluminescence (PL) and cathodoluminescence (CL) is performed for the needle-like diamond crystallites. These individual diamond crystallites were obtained by selective oxidation of polycrystalline films produced by plasma enhanced chemical vapor deposition (PE CVD). Two types of diamond films were produced with different composition of gaseous medium. For the first type, gas mixture consisted only of hydrogen and methane during the whole process. And for the second type, nitrogen was injected into the same hydrogen-methane gas mixture during a short time in the middle part of the deposition process. The samples of the needle-like diamonds, produced in these two types of CVD, were studied to determine their PL and CL spectra and spatial distribution of the luminescence intensity at various wavelengths. The characteristics of obtained PL and CL spectra indicate presence of luminescence centers related to nitrogen and silicon impurities in the diamond crystallites. The detected spatial distribution and spectral features of the luminescence are explained by variation of structural perfection at near-surface region of the crystallites.

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1. Introduction

It is known that a vast variety of luminescent centers exists in diamond crystals, including those related to crystal defects, presence external impurities and vacancies [1]. Special interest has been attracted recently to some of these luminescent centers in diamond due to their potential application in quantum optical technologies [2,3]. For example, the nitrogen-vacancy (NV) centers in diamond are considered as a promising candidate for solid state quantum bit (or qubit) [4], optical probes of magnetic [5] and electrical [6] fields, bio-marking and tracking [7]. Controllable shape, size and localization of the centers are among the highest demands to diamond materials required for these quantum optical applications. Necessary geometrical isolation of individual

luminescent centers have been demonstrated using top-down nanofabrication technique, providing structurization of single crystal diamond surface [8], as well as with self-assembling (i.e. down-top technique) of small size diamond crystallites of nanometer range (nanodiamonds) [9] where isolated color centers may be created, for example, by impurities diffusion [10]. However practical applicability of these achievements remains challenging because of low reproducibility and very limited range for variation characteristics of produced material. A benefit of chemical vapor deposition (CVD) is a comparatively easy production of diamond films for different practical applications, but extreme efforts are required to reduce the density of structural defects and occasional impurities to fabricate materials appropriate for the quantum optical applications (see e.g. [11]).

In recent reports we proposed a technology for mass production of single crystal diamond crystallites with geometrically perfect pyramidal shape [12,13]. This technology allows production of the diamond pyramidal needles with geometrical parameters

* Corresponding author at: University of Eastern Finland, Department of Physics and Mathematics, Joensuu 80101, Finland.

E-mail address: obraz@polly.phys.msu.ru (A.N. Obraztsov).

(length, base size, pyramid angle, curvature at apex), which can be varied in a controlled manner in certain range. It is important that the crystallites obtained after selective oxidation of polycrystalline CVD films have relatively high structural perfection because defective part of the films is eliminated efficiently during the oxidation. The geometrical shapes and size of the diamond crystallites allow their usage, for example, as nano-probes in scanning microscopy [14]. In this work we are analyzing luminescent properties of the single crystal diamond needles, obtained by selective oxidation of CVD films, to evaluate their applicability for optical applications.

2. Materials and methods

The samples investigated in this work were produced using combination of CVD and selective oxidation as it was described in details elsewhere [12–14]. Briefly, at the first stage of the production process polycrystalline (001) textured films consisting of micrometer scale diamond crystallites surrounded by smaller size diamonds (sub-micrometer and nanometer size) were grown on standard Si (001) substrates using direct current (DC) discharge plasma enhanced CVD method. At the second stage the CVD films were exposed to oxidation in air at temperature of about 650 °C for 20 h. The CVD parameters, that provide a stable DC discharge plasma and formation of the polycrystalline (001) textured diamond films, were found empirically: the substrate temperature of about 900 °C, total gas pressure of 9.5 kPa, gas mixture composition $\text{CH}_4:\text{H}_2=5:95$, discharge voltage of about 700 V, and discharge current density of about 1 A/cm² [12]. While the deposition time duration was 160 h for all samples, one part of them was produced without any variations in the CVD process parameters, others were produced with a single short injection of nitrogen into the reactor chamber. The injection was made by adding of 1% of N_2

into initial $\text{CH}_4:\text{H}_2$ gas mixture for 45 min at the 80-th hour of the CVD process. During the nitrogen injection, color of the DC discharge plasma has significantly varied from that it has been for the initial methane-hydrogen gas mixture. The detailed study of this variation using optical emission spectroscopy (OES) [15] is in progress now and will be reported later. Termination of the nitrogen addition leads to returning plasma discharge form (shape and color) to the initial one after complete replacement of the gaseous mixture in the reactor chamber which requires about 30 min. During this period of time nitrogen concentration in the gas mixture gradually decreased from 1% to 0%. The images obtained using scanning electron microscopy (SEM) for the cross-section cleavages of the CVD films of these two types, are shown in Fig. 1(a) and (b) and demonstrate, that nitrogen addition makes notable changes in the growth process. It should be noted also that, while the CVD films looks like rather dense and homogeneous on the cross-sectional views, in fact, they consist of well separated diamond crystallites. The largest crystallites extend through entire thickness of the film and are surrounded by small-size diamonds having similar pyramidal shape (see details in [13]). The nitrogen injection during CVD process reduces locally thickness of the largest crystallites, as it is clearly shown in Fig. 1(b).

Both types of the films were oxidized during 20 h at temperature of 600 °C in the air at normal atmospheric pressure using tubular oven. During the oxidation the most disordered fraction (including small-size diamond, graphitic and amorphous carbon) was eliminated from the films completely due to its gasification. Remaining part of the film material was represented by a white colored powder consisting of the diamond crystallites of the larger size. These crystallites were transferred onto different substrates (glass, metal, Si etc.) for further manipulation and investigation. Typical SEM images of individual diamond crystallites of micrometer size are shown in Fig. 1(c) and (d). The length of the crystallites corresponds to CVD growth rate of about 1–1.5 $\mu\text{m}/\text{h}$.

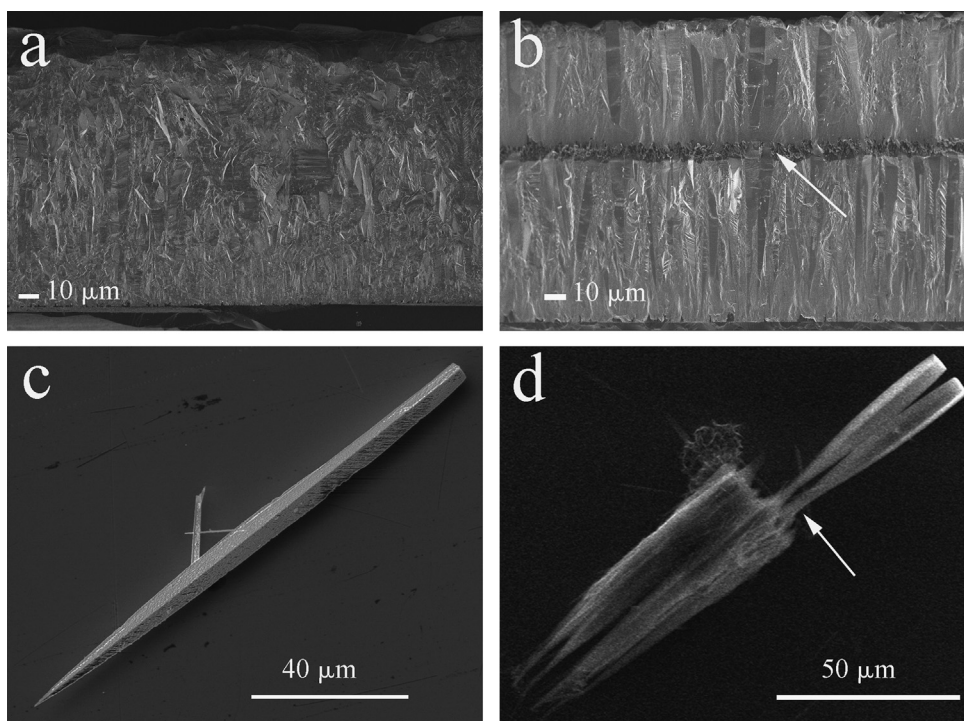


Fig. 1. SEM images of diamond polycrystalline films obtained by CVD and separate crystallites obtained by selective oxidation of the films. a – SEM image of cleavage of a sample grown at constant CVD parameters without nitrogen addition; b – SEM image of cleavage of a similar film obtained with nitrogen injection during CVD process; c – SEM image of an individual diamond crystallite obtained after selective oxidation of CVD film produced without nitrogen; d – SEM image of crystallites obtained after selective oxidation of the CVD film produced with nitrogen injection. Arrows in the images b and d indicate local reduction of the crystallite thickness corresponding to nitrogen injection during CVD. The growth directions for the crystallites, shown in the images c and d, are from bottom left to upper right corners of the images.

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