Spatial localization of Si-vacancy photoluminescent centers in a thin CVD nanodiamond film

A. A. Basov¹, M. Rähn², M. Pärs², I. I. Vlasov¹, I. Sildos*,², A. P. Bolshakov¹, V. G. Golubev³, and V. G. Ralchenko¹

¹ General Physics Institute RAS, Vavilova 39, 119991 Moscow, Russia
² Institute of Physics, University of Tartu, Riia Street 142, 51014 Tartu, Estonia
³ Ioffe Physical Technical Institute RAS, 26 Polytekhnicheskaya, St Petersburg 194021, Russia

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* Corresponding author: e-mail ilmo@fi.tartu.ee, Phone: +372 737 4613, Fax: +372 7 383 033

A nanosized island-like diamond film containing silicon-vacancy (SiV) centers was grown by microwave plasma CVD on Si substrate. The diamond film was characterized by scanning electron microscope, microRaman, and photoluminescence spectroscopies. Nonuniform spatial localization of the SiV photoluminescent centers with a density over 1/\mu m² in the photoemitting regions is found. Interfering factors hindering registration of emission from a single SiV center in thin CVD nanodiamond films are determined.

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1 Introduction Optical defects in diamond occurred to be quite promising as single photon emitters [1]. A lot of fundamental and applied research have been performed by using single nitrogen-vacancy (NV) color centers having pronounced zero-phonon line (ZPL) at 637 nm with quite strong phonon sideband due to strong electron–phonon coupling [2]. Silicon-vacancy (SiV) defects with ZPL at 738 nm and nickel-related defects with ZPL at 802 nm both have weak interaction with phonons of the host [3, 4]. The mentioned set of defects in diamond could be used as a single photon source with transform-limited coherence length of photons for quantum computing [5].

The SiV defects in diamond demonstrate high photostability and narrow-band photoemission at room temperature (RT) making them promising for application in luminescent biomarkers and single photon emitters. Wang et al. [3] succeeded in observation of single photon emission from SiV defects produced by ion implantation in bulk diamond. Recently, the conservation of high thermodynamic stability of the SiV defect when passing from a bulk crystal to diamond nanoparticles of <10 nm in size has been predicted by density functional tight-binding simulations and demonstrated experimentally for the case of continuous nanocrystalline diamond films [6]. This finding opens the door for the development of single photon emitters based on SiV defect photoluminescence (PL) in CVD nanodiamond (ND). The developing can move forward in two directions. First one is obtaining the isolated diamond nanoparticles with single SiV defect by disintegration of relatively thick continuous ND films onto individual crystallites. Second direction is the formation of spatially localized SiV defects in ND grains grown on substrate directly during growth process. To get desirable density and spatial distribution of the optical centers a systematic study of the density and the distribution dependencies on growth parameters: deposition time, density of seeding, level of Si doping, etc., is required in this approach.

In the present work, we studied a distribution pattern of the photoluminescent SiV centers in a thin (ca. 20 nm thickness) CVD ND film grown at high seeding density and doped with Si from silicon substrate. Interfering factors hindering registration of the emission from a single SiV center in thin CVD ND films were clarified.

2 Experimental The nanocrystalline diamond film has been grown in a microwave plasma CVD reactor
on $10 \times 10 \times 0.5$ mm$^3$ mirror-polished Si substrate using 3% CH$_4$/97% H$_2$ gas mixture at the following conditions: substrate temperature 850 °C, pressure 87 Torr, gas flow rate 500 sccm, microwave power 3.4 kW, and deposition time 3 min. Before the deposition the substrate was seeded with ultradispersed diamond (UDD) clusters of detonation synthesis using a special aerosol-plasma technique. This technique assumes formation of UDD jet bombarding the substrate to provide high density ($\sim 10^{10}$ clusters/cm$^2$) and uniformity of the seeding. Silicon doping of the diamond was realized through the chemical etching of the substrate in the plasma at the first stage of the deposition process (when the diamond film remains island-like), Si atoms and/or SiH$_x$ species then incorporating from plasma to growing crystallites.

Morphology and thickness of the film were characterized by imaging of the film with scanning electron microscope (SEM) JSM-7401F (JEOL). For optical characterization of samples a microRaman/luminescence spectrometer from Renishaw was used. Spatial micromapping and separation of bright optical emitters in films were performed by homemade confocal microscope equipped with an XYZ motorized scanning stage. For optical excitation the emission from a laser diode operating at 488 nm was used. The motivation to use this excitation wavelength was to eliminate the probable PL background from NV centers. Luminescence from a spatially confocal volume was either split into two parts and detected by two avalanche photodiodes (APD) for correlation measurements or sent to single grating spectrometer (Shamrock i301 equipped with Newton EMCCD) to perform the spectral measurements. The APD were also configured as a Handbury-Brown-Twiss interferometer for characterizing the photon state of emission to check how many emitters were involved into the nanoislands. The laser radiation was blocked by using an interference edge filter (redpass from 664 nm, Semrock LP02-664RS-25) and fluorescence was selected by red narrow bandpass interference filter.

3 Results and discussion A typical SEM image of the diamond film surface is shown in Fig. 1. It is seen that the Si substrate is uniformly covered with ND islands of sizes varied in the range of 10–100 nm. A closer inspection reveals that the islands are composed of smaller grains with average size of about 12 nm, so the diamond nucleation density was as high as $3 \times 10^{11}$ cm$^{-2}$. Cross-section SEM imaging of the film gave us characteristic thickness of the film of 15–20 nm. In case of a more prolonged growth process (10 min) a continuous diamond film of 200 nm thickness with well-faceted crystallites was formed.

Probing of PL with 488 nm laser beam of $\approx 1$ μm in diameter in different points of the island film surface revealed nonuniformity in a distribution of the PL emission intensity from SiV centers on a micrometer scale. There were regions of a square in few micrometers within which no SiV emission was observed at all, whereas within other few-micrometers-sized regions an intensity of the SiV emission varied in a few times from point to point. Combined Raman/PL spectrum of the film excited at 488 nm laser light with the strongest signal from SiV centers is shown in Fig. 2. The Raman spectrum for the ND film consists of the three lines indicating the presence of diamond (the narrow peak at 1332 cm$^{-1}$) and amorphous carbon (two broad bands at 1350 cm$^{-1}$ (D) and 1570 cm$^{-1}$ (G)). The PL spectrum shows only the doublet of ZPL from SiV centers at 738 and 757 nm. Note the absence of lines at 575 and 638 nm wavelengths related to NV centers in the nanocrystalline diamond film of $\approx 20$ nm thickness.

To investigate the spatial distribution of fluorescence intensity in the range of maximum emission from SiV centers in more detail, the confocal mapping at 658 nm laser excitation was performed. The narrow-spectral-range fluorescence was selected by red bandpass filter (Omega Optical 3RD720-760) with center wavelength of 740 nm and bandwidth of 40 nm. Mapping image is shown in Fig. 3. A distribution of the emission intensity around 738 nm is similar to that observed at 488 nm laser excitation as described above. The image consists of few-micrometers-sized regions one of which do not emit at 738 nm and others emitting with variable intensity within the region. Note that besides expected emission from SiV centers the

Figure 1 SEM image of the ND film.

Figure 2 Combined Raman/PL spectrum of the CVD ND film, measured at RT ($\lambda_{ex} = 488$ nm).
Figure 3 (online color at: www.pss-a.com) Image of confocal fluorescence mapping of CVD ND film at RT; 658 nm laser excitation was used. Fluorescence is selected by the red bandpass filter (center wavelength of 740 nm and bandwidth of 40 nm). Blue–red–white is a color sequence corresponding to the increase of the emission intensity.

Raman scattering from amorphous carbon (G line) was also contributed into the bright emission is shown in Fig. 3. Typical PL spectra recorded from two different spots without bandpass filter at 658 nm laser excitation are shown in Fig. 4. The 738 nm line from SiV defects dominates in the filter bandpass region of the upper PL spectrum, while G band from amorphous carbon dominates in that region of the lower PL spectrum in Fig. 4. Besides the first and second order silicon Raman lines (520.5 and 963 cm$^{-1}$, respectively) coming from the substrate are present in both spectra in Fig. 4. Substantial quantity of nondiamond carbon is the characteristic for initial stage of CVD diamond growth [7]. Observation of the bright spots in the PL image of the ND film associated with a strong signal (G band) from amorphous carbon demonstrates high nonuniformity in distribution of the amorphous carbon within the film on a micron scale.

The Handbury–Brown–Twiss interferometry was used for characterization of the photon state of those bright spots, which were related to SiV emission. It was found that the photon statistics does not show any deviation from poissonian indication presence of multiple color centers in laser focus. Two main factors could explain this result. The first one is essential wide-band structureless background observed in PL spectra of the film at 658 nm wavelength excitation (seen clearly in the inset of Fig. 4). Clarification of the origin of this background is in progress. An integral intensity of the background in the filter bandpass region is about two times higher than integral intensity of the SiV emission. The second factor is a presence of a few SiV defects within the laser probing volume of the film. Variable intensity of the emission from fluorescent regions confirms this assumption.

4 Conclusion A spatial localization of the photoluminescent SiV centers in a thin (ca. 20 nm thickness) CVD ND film grown at high seeding density and doped with Si from silicon substrate was studied. It was found that in spite of the uniform high dense covering of the Si substrate with diamond nanoislands, the emission from SiV centers is not uniformly distributed within the film surface at micrometer level. Further study of the reasons of such nonuniformity is required. In the fluorescent regions a density of the emitting centers is higher than 1/μm$^2$.

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