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Luminescent properties of individual Silicon-Vacancy centers in CVD nanodiamonds grown on various substrates

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The application of the technique of resonant excitation of photoluminescence at low temperatures using a narrow-band tunable laser significantly expands the possibilities of spectral investigation of individual luminescent centers in nanodiamonds, even in conditions of high concentrations of such centers. In this paper, a comparative analysis of the spectral characteristics of individual „Silicon-Vacancy" (SiV) centers in nanodiamonds grown with a spontaneous nucleation technique on germanium and silicon substrates is carried out. Studied diamond nanoparticles have a characteristic size of 300 nm and contain large ensembles of SiV centers. It was found that during the transition from silicon substrates, which are traditionally used in the CVD synthesis of diamonds, to germanium substrates, the spectral characteristics of the photoluminescence of SiV centers almost do not change.

Keywords: nanodiamonds, luminescence, „Silicon-Vacancy", resonant excitation.

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1. Introduction

Negatively charged Silicon-Vacancy centers (SiV), along with other luminescent point defects in diamond, are extremely popular sources of both single-photon and classical radiation in the visible spectral region, respectively, for quantum and biomedical technologies. The most common method of synthesis SiV-containing diamonds is Chemical Vapor Deposition (CVD) method. Typically, in the CVD synthesis of individual diamond particles and polycrystalline films, pre-seeding of the substrate on which the synthesis takes place with ultra-small diamond nanoparticles is used. Recently, to obtain luminescent diamond nano and microparticles, scientific groups from Russia and France have been actively developing alternative approaches based on spontaneous diamond nucleation under CVD synthesis [5,6], conditions, which was first described in the work of Professor B.N. Spitsyn et al. [7]. In the present work, a comparative analysis of the spectral characteristics of individual SiV centers in nanodiamonds grown in the spontaneous nucleation mode on germanium and silicon nm substrates was performed. The studied nanoparticles have a characteristic size of 300 nm and contain large ensembles of SiV centers. Nevertheless, the low temperature (15 K) and resonant laser excitation of luminescence make it possible to characterize individual SiV centers.

2. Experimental methods

Synthesis of silicon-doped nanodiamonds (ND) was performed in a microwave CVD reactor „ARDIS-100" (Optosystems Ltd.). Polished Si (100) and Ge (111) wafers were used as substrates. For convenience, we will call ND grown on silicon — „Si"-ND, and those grown on germanium — „Ge"-ND. Both types of samples were grown in the mode of spontaneous diamond nucleation on the surface of germanium and silicon substrates [6]. To stimulate diamond nucleation on the Ge surface, the substrates were treated in a 25% aqueous ammonia solution before synthesis: the substrates were dipped into the ammonia solution for a few seconds, then washed in distilled water and dried. A methane/hydrogen gas mixture at a pressure of 75 Torr was used for ND synthesis. In preliminary experiments, we found that the maximum possible nucleation density of diamond particles on both substrates is achieved at the volume ratio $CH_4/H_2 = 6\%$ This is the ratio that was chosen for the ND synthesis. The temperature of the substrates during ND growth was measured with a Micron M770 pyrometer. The formation of SiV centers in „Si"-ND was carried out mainly by uncontrolled etching of the Si substrate in hydrogen plasma. In the „Ge"-ND sample, SiV formation occurred by adding a small amount of silane (SiH_4) to the methane-hydrogen mixture, which allowed us to control the formation of luminescent centers in this sample. The main parameters of CVD ND growth on two different substrates are shown in the Table 1.

Table 1. CVD synthesis conditions

Substrate	Pressure gas, Torr	Power plasma, kW	CH_4/H_2 %	Source Si, %	Time growth, min	Temperature substrate, C°
Si	75	3	6	Etching of silicon substrate	15	850
Ge				$CiH_2/CH_4 = 0.1$	20	800

A Jeol 7001F scanning election microscope (SEM) was used to determine the morphology and lateral size of the grown ND.

The photoluminescence (PL) spectral characteristics of SiV centers were investigated at cryogenic temperatures in non-resonant and resonant laser excitation modes. In the first mode, the PL was excited by a diode laser at a wavelength of 660 nm (L660P120, Thorlabs). The second mode used a tunable continuous Ti:Sapphire laser (Solstis, M Squared) with a line width of less than 5 MHz and a tunable emission wavelength range of 700 to 800 nm.

For cooling, the sample was placed in a closed-loop cryostat chamber (attoDRY 800, Attocube). The sample holder temperature stabilized at 15.0 ± 0.1 K. The cryostat was combined with a homemade confocal scanning microscope. The pumping laser beam was focused on the sample using a cryo-compatible microscope lens ($\times 100$, $NA = 0.82$, Attocube). The position of the pumping laser beam on the sample was controlled using a galvo mirror (FSM 300, Newport). The PL signal was collected in a single-mode fiber (SM600, Thorlabs) and then sent either to a single-photon avalanche photodetector (SPAD, SPCM-AQRH-15, Perkin Elmer) or to a spectrometer (IsoPlane 160, 0.07 nm resolution, Princeton Instruments). In the experiment with resonant excitation, the PL spectra were recorded based on the dependence of the intensity of the phonon component of the PL ($\sim 30\%$ of the total emission), which was extracted using filter sets in the $750-795$ nm range, on the wavelength of the excitation radiation in the $700-750$ nm range. For express recording of resonance spectra, the step size was 500 MHz, for recording of high resolution spectra — 40 MHz.

The second-order autocorrelation function $g^2(\tau)$ was determined with a standard Brown-Twiss interferometer using a time-digital converter (quTAU) with a temporal resolution of 81 ps.

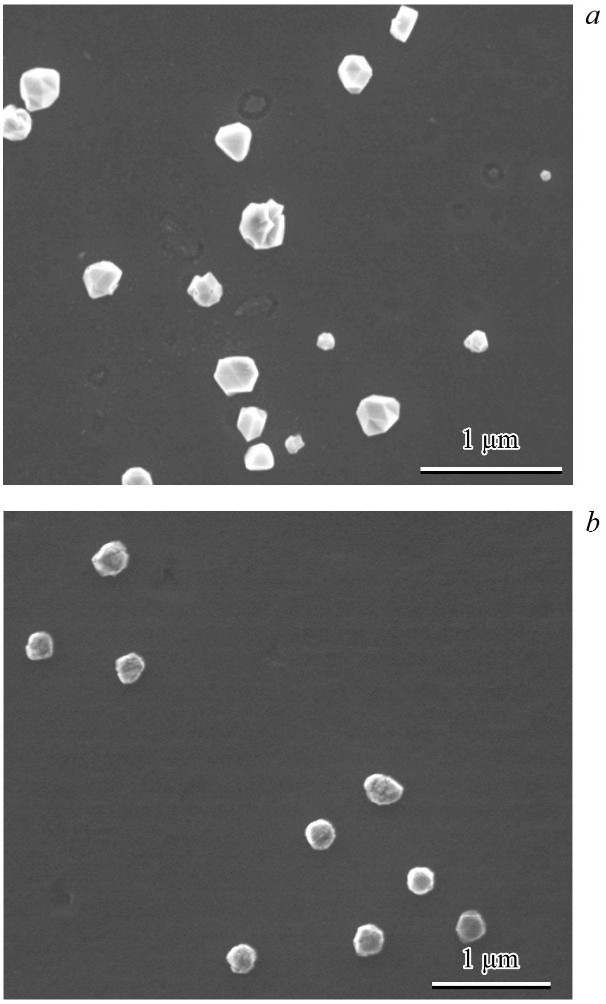

Figure 1. SEM images of NDs grown by the CVD method on Si (*a*) and Ge (*b*) substrates.

3. Results and Discussion

3.1. SEM microscopy

The ND synthesis time was chosen so that the characteristic sizes of individual diamond particles on both substrates were close to 300 nm. This size was chosen for the convenience of optical imaging and identification of investigated particles during the transition from one method of their characterization to another. SEM images of the analyzed samples confirm that the NDs grown on Si and Ge substrates have a characteristic size of about 300 nm (Fig. 1, *a* and 1, *b*, respectively). Note that the morphology of Ge“-ND particles slightly differs from that of Si“-ND: particles with a polycrystalline structure prevail on the Ge substrate, whereas NDs with a well-defined singular facet, i. e., mono-crystals, dominate on the Si substrate.

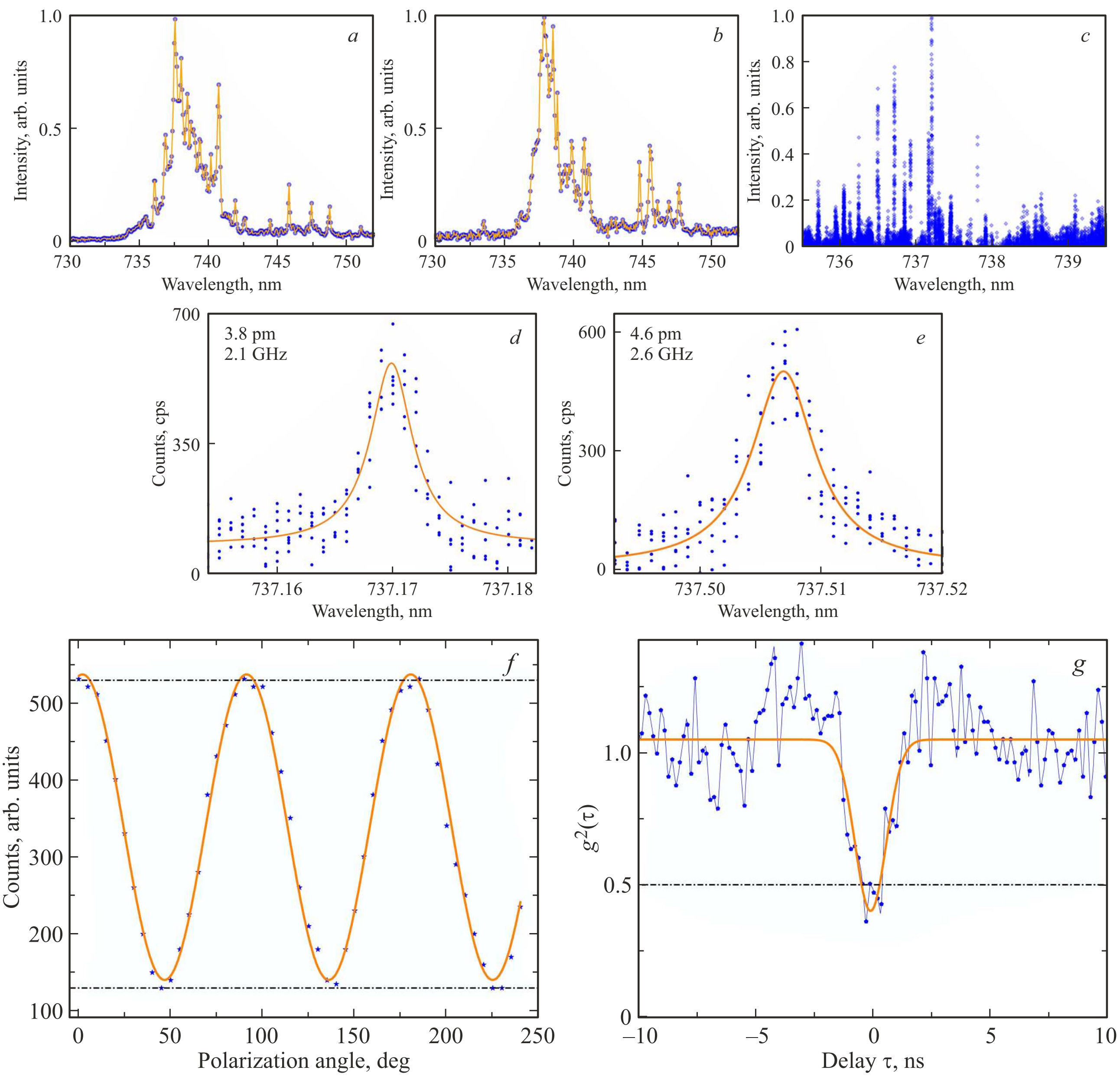

Figure 2. Characterization of the luminescence properties of individual SiV color centers in NDs at low temperature. Non-resonant excitation by 660 wavelength continuous laser for a single diamond nanoparticle of about 300 wavelengths on Si (*a*) and Ge (*b*) substrates. Example of a characteristic PL (*c*) spectrum recorded at a large scanning step with resonant laser excitation, in the spectral range 735–740 nm. Profiles of SiV lines of individual centers in NDs on Si (*d*) and Ge (*e*) substrates, recorded with high spectral resolution by resonant laser scanning. Polarization sensitivity (*f*) of the single SiV line presented in the inset (*e*). Second-order autocorrelation function $g^2(\tau)(g)$ confirming addressable spectral reversal to a single-photon SiV source, with spectrum (*e*) under resonant laser excitation. All experimental data presented in the plots (*a*–*g*) are represented by blue dots, while in the cases (*a*) and (*b*) the experimental data are connected with orange lines for clarity, for plots (*d*–*g*) orange contours represent approximation dependencies.

3.2. PL spectroscopy at low temperature

Before cooling, the PL spectra of the samples were recorded at room temperature under laser excitation at a wavelength of 532 nm. It was found that the ratio of the peak intensity of the SiV zero-phonon (ZPL) line near 738 nm to the intensity of the diamond Raman scattering line (at raman frequency of 1332 cm^{-1}) for a number of investigated nanoparticles on both substrates varied from 2 to 7, which indicates a close degree of silicon doping of both samples ND.

The characteristic PL spectra recorded in the mode of non-resonant laser excitation with a power of 1 mW at a wavelength of 660 nm at 15 K for individual particles on „Si"-ND and „Ge"-ND are shown in Fig. 2, *a* and

2, *b*, respectively. The spectra show many non-overlapping and overlapping narrow lines in the $735-750$ nm range, indicating a high SiV center content in a single 300 nm particle. The variation in the frequencies of individual SiV-emitters within one particle is explained by the presence of internal local stresses [6] in it. This fact facilitates the observation of luminescence lines from individual SiVs even when working with sufficiently large ensembles of these centers. Nevertheless, the spectral resolution of the spectrometer (0.13 nm) used to record SiV PL under non-resonant excitation is much higher than the minimum possible line width (~ 100 MHz) from individual SiVs, which does not allow to study their spectral characteristics in detail.

The application of the resonant PL excitation technique using a narrow-band tunable laser with a line width of 5 MHz significantly expands the possibilities of spectral study of individual SiV centers. The PL spectrum recorded with a large scanning step (see Section 2 for details) at resonant excitation in the 735–740 nm range is shown in Fig. 2, *c*. Note that the spectra in Figs. 2, *b* and 2, *c* are shown for the same particle ND on Ge. There is much less overlap between individual lines than in the case of non-resonant excitation: the lines with the smallest widths most likely belong to individual SiV centers.

Fig. 2, *d* and 2, *e* show spectra obtained with a small scanning step for the narrowest luminescence lines in „Si“-ND and „Ge“-ND samples, respectively. The spectra were recorded at the maximum resonant excitation power that does not cause spectral line broadening due to sample heating: about 100 nW. The approximation of the SiV lines by the Lorentz profile shows that their FWHMs are close for both samples and are about 2.1 GHz (for Si) and 2.6 GHz (for Ge).

To prove that the selected SiV lines really correspond to single emitters, we analyzed their polarization sensitivity (Fig. 2,*f*) and measured the second-order autocorrelation function $g^2(\tau)$ (Fig. 2, *g*). For polarization measurements, a half-wave plate was used to rotate the polarization angle of laser radiation in the sample plane. For an individual SiV center, being a radiating dipole, a sinusoidal change in the intensity of the observed luminescence with a change in the angle of polarization of the excitation radiation is expected. Indeed, the PL line shown in Fig. 2, *e* exhibits high polarization sensitivity (Fig. 2,*f*). For the same SiV line, the measured depth of the second-order autocorrelation function failure exceeded 50%, which satisfies the criterion of a single-photon source (Fig. 2, *g*).

We should also note the extremely high photostability of the studied SiV lines: their short-term flicker is insignificant, the initial intensity level is retained for tens of hours of laser irradiation.

4. Conclusions

A comparative analysis of the characteristic spectral positions and luminescence line widths of individual SiV centers within one diamond nanoparticle was performed for ND samples grown by the CVD method on germanium and silicon substrates. It was shown that the photoluminescence spectral characteristics of SiV centers practically do not change when switching from silicon substrates, which are traditionally used in CVD synthesis of diamonds, to germanium substrates. At the same time, the use of Ge substrates, which have weak adhesion to diamond, opens up new possibilities in the formation of SiV centers and their applications: it allows controlled doping of ND with silicon, facilitates the transfer of diamond particles from the growth substrate to optical chips, microresonators, photonic crystals and other photonic circuits. Note also that individual SiV centers formed in CVD-diamond nanoparticles (due to their high photo-stability and fairly narrow luminescence line width) are promising candidates for creating single photon sources based on them, operating at room temperatures.

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Conflict of interest

The authors declare that they have no conflict of interest.

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