Conference materials
UDC 535-4
DOI: https://doi.org/10.18721/JPM.161.323

Enhancing single-photon emission of silicon-vacancy centers in nanodiamonds by a gold film

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Abstract. In this work, the single-photon emission of SiV-centers in HPHT-nanodiamonds positioned on the surface of silicon plate and gold film was investigated. Fluorescence spectra, saturation curves and fluorescence decay curves were measured for a number of SiV-emitters. A reduction in the fluorescence lifetime by ~20%, as well as a spectral shift and a decrease in the width of the zero-phonon line of SiV fluorescence were observed for most emitters. Analysis of the saturation curves revealed an increase in the emission rates by an average of 3 times, and up to 13 times for some particles. The wide variation is primarily associated with the orientation of the dipole moment of the SiV centers and the size of diamond particles, which are the key parameters regulating the coupling of the emitter with surface plasmons in the gold film.

Keywords: nanodiamonds, color centers, single photon, fluorescence, plasmonics

Funding: The study was supported by the Russian Science Foundation grant 22-19-00324.

Citation: Romshin A.M., Gritsienko A.V., Ilin A.S., Bagramov R.K., Filonenko V.P., Vitukhnovsky A.G., Vlasov I.I., Enhancing single-photon emission of silicon-vacancy centers in nanodiamonds by a gold film, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 16 (1.3) (2023) 135–139. DOI: https://doi.org/10.18721/JPM.161.323

Материалы конференции
УДК 535-4
DOI: https://doi.org/10.18721/JPM.161.323

Усиление однофотонной эмиссии кремний-вакансионных центров в наноалмазах с помощью золотой пленки

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Аннотация. В настоящей работе исследовалась однофотонная эмиссия кремний-вакансионных центров в HPHT-наноалмазах, расположенных на поверхности кремния

и золотой пленки. Для каждой из частиц записывались спектры люминесценции, измерялись кривые насыщения и кривые затухания флуоресценции. Для большинства эмиттеров было обнаружено сокращение времени жизни флуоресценции на ~20%, а также зафиксирован спектральный сдвиг и уменьшение ширины бесфононной линии флуоресценции кремний-вакансионных центров. Анализ кривых насыщения позволил обнаружить увеличение скорости однофотонной эмиссии в среднем в 3 раза, а для некоторых частиц – до 13 раз. Широкий разброс связан с ориентацией дипольного момента кремний-вакансионных центров и размером алмазных частиц, являющимися ключевыми параметрами, регулирующими взаимодействие эмиттера с поверхностными плазмонами в золотой пленке.

Ключевые слова: наноалмазы, центры окраски, однофотонная эмиссия, плазмоника

Финансирование: Работа выполнена при поддержке гранта РНФ № 22-19-00324.

Ссылка при цитировании: Ромшин А.М., Грициенко А.В., Ильин А.С., Баграмов Р.Х., Филоненко В.П., Витухновский А.Г., Власов И.И. Усиление однофотонной эмиссии кремний-вакансионных центров в наноалмазах с помощью золотой пленки // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2023. Т. 16. № 1.3. С. 135–139. DOI: https://doi.org/10.18721/ JPM.161.323

Introduction

In recent decades, optical quantum networks rapidly progress in the direction of information processing and transmission [1, 2]. An indispensable building brick for realization of such devices is single photon emitter (SPE) that should meet the requirements of high spectral purity, unprecedented brightness and directivity of radiation. One of the most promising solid-state SPE is the silicon-vacancy (SiV) diamond color center, which has an intense and narrow zero-phonon line (ZPL) at ~738 nm, as well as high spectral and temporal stability [3, 4]. This center possesses near nanosecond fluorescent lifetime resulting in high emission rates with low phonon-mediated acts of emission – more than 70% of total emission is concentrated in ZPL. To improve optical properties and primarily detected count rates the emitters are typically coupled to different microcavities which are aimed to increase local density of optical states and modify the directivity of emission. Many approaches are used for these purposes, including dielectric Fabry-Perot microcavity [5, 6], photonic crystals [7], metasurfaces [8], plasmonic nanoantennas and microstructures [9, 10]. However, despite numerous studies of complex structures, the behavior of single photon emitters even in simple diamond-on-metal systems is still not entirely unclear.

In this paper, we comprehensively study the single photon emission of SiV-centers in HPHT-produced nanodiamonds positioned on the silicon and gold surfaces. By means of confocal spectroscopy and Hanbury-Brown-Twiss interferometry, the fluorescence spectra, saturation curves and decay times of SPE were measured for ten different NDs and the results were quantitively compared for those two surfaces. Such a plain “diamond-on-metal”-structure revealed more than order enhancement of fluorescent signal.

Materials and Methods

The NDs under study were synthesized by high-pressure high-temperature (HPHT) method from a mixture of adamantane ($C_{10}H_{16}$) and detonation nanodiamonds at a pressure ~7.5 GPa, temperatures 1600–1700 °C and time exposition 20 s. To form SiV-centers in diamond matrix a small amount of tetrakis(trimethylsilyl)silane ($C_{12}H_{36}Si_5$) was added to final mixture with the ratio ~Si/(Si+C) = 0.0001%. The 0.1 mg of output ND-powder was diluted in 2 ml of ethanol and then sonicated in ultrasonic bath during 30 min to form homogeneous suspension of NDs. Eventually, 2 μl of the resulting suspension was applied to both silicon and gold surfaces. Pre-characterization in scanning electron microscope (SEM) revealed the size distribution of NDs between 150 nm and 500 nm.

Optical properties of NDs were studied in a home-built confocal microscope equipped with two laser sources, continuous at 660 nm and pulsed at 630 nm ($\tau_{pulse} \sim 80$ ps). To prove the single photon nature of color centers, an emission Hanbury-Brown-Twiss (HBT) interferometer with two avalanche photodiodes (APDs, Excelitas SPCM-AQRH-14-FC) was used. The fluorescence spectra were recorded with an Ocean Insight QEPro spectrometer, and for saturation measurements the APDs with a band pass filter (728–749) were employed. Notice that a long-distance objective Mitutoyo ×100, NA = 0.7 was used in all these measurements. The fluorescence decay rates were analyzed with a Picoquant MicroTime 200 time-correlated single photon counting (TC SPC) module and Olympus lens (×100, NA = 0.95).

Results and Discussion

First, we chose ten random NDs emitters on each of the two substrates – silicon and gold – whose emission is satisfied to criteria of the single photon statistics. An identification of such sources was carried out by measuring the second order autocorrelation function $g^{(2)}(\tau)$ for SiV emission. Fig. 1, *a* demonstrates an example of $g^{(2)}(\tau)$-functions for NDs on silicon (ND-S) and gold (ND-G). The dip at zero time-delay ($\tau = 0$) is less than 0.5 indicating a subpoissonian statistics of light and consequently its single photon nature.

Next, the fluorescence spectra were recorded for selected NDs (Fig. 1, *b*). The narrow line near 738 nm corresponds to the ZPL of the SiV-fluorescence. For each emitter the spectral position (λ_{center}) and full width at half maximum (FWHM) of the ZPL were determined (Fig. 1, *c*). The set of red dots (ND-Ss) is concentrated primarily in short-wavelength range with $\langle \lambda^{Si}_{center} \rangle = 738.7$ nm and $\langle \Delta\lambda^{Si} \rangle = 3.9$ nm. However, some points are far away from mean values (e.g., ~741 nm) which may be explained by the local intrinsic stress in diamond lattice [4]. In contrast, the ZPLs for ND-Gs (blue dots) are narrower on average by factor of 1.7 and red-shifted with $\langle \lambda^{Si}_{center} \rangle = 739.1$ nm. Although the distribution spread is wider for ND-Gs, we believe some of them could be effectively coupled with surface plasmon in gold film resulting in ZPL shift and narrowing.

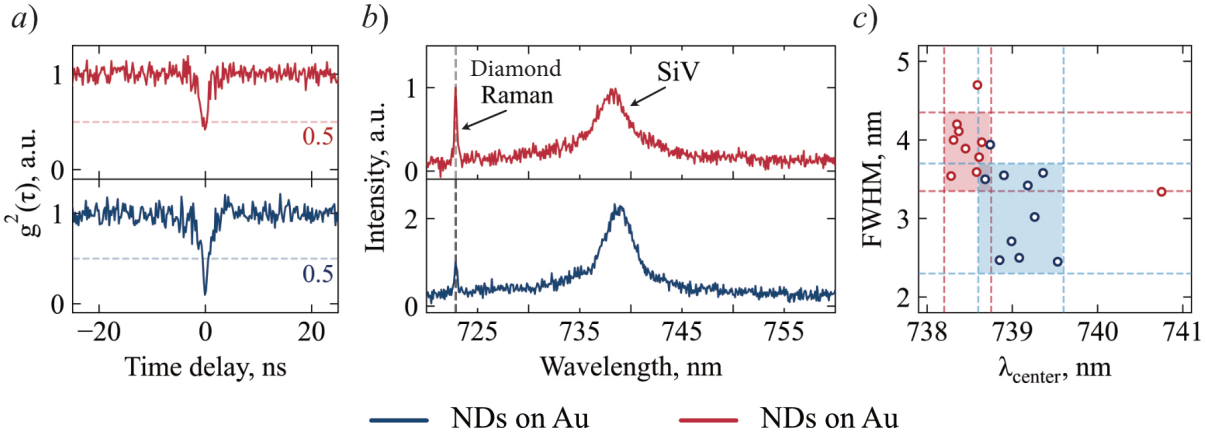

Fig. 1. Optical properties of the emitters in NDs placed on silicon substrate (red) and surface of gold film (blue): a second order autocorrelation function $g^{(2)}(\tau)$ for two NDs (*a*); an instance of fluorescence spectra for two distinct NDs (*b*); post-processing of ZPL λ_{center} and FWHM for ten points for NDs on silicon and gold (*c*).

All data were obtained at 3 mW (before objective) power of continuous 660 nm laser source

To quantify the comparison between ND-Gs and ND-Ss the saturation measurements were performed. For clarity, saturation curves for three NDs on each substrate are demonstrated in (Fig. 2, *b*). The dependences can be described as $I(P) = I^{\infty} \cdot P/(P + P^{sat})$, where I^{∞} is the peak count rate in the limit of large P, P^{sat} is the saturation power. The values I^{∞} and P^{sat} obtained for different NDs on the silicon and gold are presented in (Fig. 2, *c*). One can see the superiority of the emission rate for ND-Gs in high power limit by an enhancement factor (EF) of 3.1 while the EF for distinct emitters reaches the value of $EF_{max} = 13$. The saturation power on average decreases from $\langle P^{sat}_{Si} \rangle = 46.1$ mW to $\langle P^{sat}_{Au} \rangle = 23.9$ mW reflecting an increased extinction of excitation power for ND-Gs.

We also performed time-resolved fluorescence intensity measurements for the NDs (Fig. 2, *a*). The fluorescence decays for ND-Ss demonstrate mono-exponential behavior. In contrast, for ND-Gs deeply sub-ns component was revealed which we believe is not related to SiV-fluorescence, but rather to a diamond-enhanced background from the gold surface [11]. The SiV-fluorescence decay times extracted from the decay curves were averaged over ten NDs and compared between each other. The relaxation time reduces by ~20% on average for emitters on gold surface.

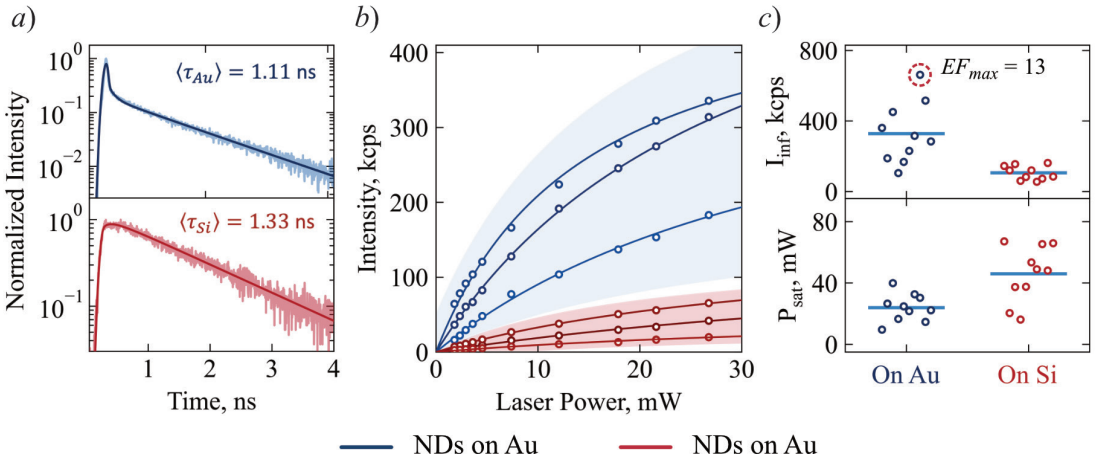

Fig. 2. Decay curves measurements for NDs on silicon (red) and gold surfaces (blue) (*a*). The insets show the decay times averaged over ten NDs on both silicon and gold. Excitation power dependences of the ZPL intensity for three random NDs on different substrates (*b*). The shadow regions illustrate typical scopes for the rest NDs not presented on the graph. Extracted I^{∞} and P^{sat} for ten NDs on both silicon and gold surfaces (*c*). Light blue bars indicate the averaged over ten emitters values

The wide spread of the EF obtained for ND-Gs could be explained by analyzing the major mechanisms affecting the EF. First, observed changes in fluorescence lifetime do not cover the gap for bright emitters (e.g., $EF_{max} > 5$), therefore the Purcell enhancement of spontaneous emission is only minor contributing factor. Second, the P^{sat} reduction hints on increased extinction of excitation power resulting in more effective (by a factor of ~2) photoexcitation of the SiV-centers. The possible reason for this behavior is the size distribution of the NDs which covers a part of the range where Mie-resonances take place. Finally, we believe the dipole orientation relative to the surface normal plays a crucial role in the pronounced enhancement leading to more efficient extraction of the fluorescence signal and resonant interaction with surface plasmon mode in gold film which is partially confirmed by alterations of ZPL spectral characteristics.

Conclusion

In summary, the fluorescent properties of the single SiV-centers in HPHT nanodiamonds on silicon and gold surfaces were studied. Such simple system diamond-on-metal demonstrates an enhancement of SiV-fluorescence by more than an order of magnitude. Relying on the spectral and fluorescent decay measurements we relate the major contribution to the enhancement to the orientation of dipole moment and its coupling to the surface plasmon in gold film. The results obtained serve as a good starting point for the development gold nanocavities and antennas with consequent nanodiamonds integration for the state-of-the-art nanophotonic applications.

Acknowledgments

R.K.B. and V.P.F. synthesized nanodiamonds, A.S.I. prepared silicon substrates and gold film, A.M.R. performed confocal saturation and spectral measurements, A.V.G. measured the fluorescent decay rates, A.M.R. processed the data, prepared illustrations and develop the draft of the manuscript, A.G.V. and I.I.V. supervised the direction of the study. All authors contributed to conceptualization of the study and reviewing of the manuscript.

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Received 14.12.2022. Approved after reviewing 23.01.2023. Accepted 06.02.2023.