Creation and investigation of quantum emitters in nanodiamond structures

FINAL REPORT

Foreword

The production of reliable and scalable quantum emitters is a key parameter for light-based quantum information technology and nanophotonics related applications, since the generation and manipulation of the photons on a single level is very crucial for these technologies. Among several competitors, diamond-based point defects or so-called color centers are one of the most promising objects. The benefits of these structures lie in the unique physical and chemical properties of the diamond matrix itself and in the variety of impurities able to form optically active point defects with fascinating optical properties, that can operate even at room temperature [1, 2].

There are several types of impurity-related point defects that show single photon emission capability. The nitrogen-vacancy (NV) center was the first experimentally proved one. However, several practical insufficiencies of the NV center, like the strong electron-photon coupling of the defect (which appears as a very broad and intense phonon sideband in the photoluminescence (PL) spectra), or low Debye-Waller factor (only a small, 0.04% part of the emission is concentrated in the main optical transition (Zero-Phonon Line - ZPL) of the defect), and charge state instability (fluctuation between neutral NV^{o} and negatively NV^{-} charged states) initiated intense research to create color centers in diamond that overcome the mentioned weaknesses of the NV defect.

The aim of this, mainly experimental, research project was to produce and study metalloid-related color centers (mainly silicon- (SiV) and germanium-vacancy (GeV) defects) containing diamond nanostructures appropriate for use as a single photon source and enhance their emission properties.

1. Creation of SiV and GeV center containing diamond nanostructures by impurity-assisted CVD

There are numerous methods capable of producing optically active point defects in diamond nanostructures. These include but are not limited to the different impurity-assisted high-pressure high-temperature (HPHT) or chemical vapor deposition (CVD) synthesis and the ion implantations or laser-assisted posterior doping techniques. The impurity-assisted CVD growth has several benefits compared to other techniques: it allows to introduce impurity atoms during the growth of the diamond structures without destroying the crystalline structure; the morphology and the properties of the diamond structures can be tuned in a wide range by changing the growth parameters; additional treatments for structural relaxation or surface functionalization can be applied within one process, if required; the size of crystals and type of the structure can be controlled, which is essential to produce diamonds on micro- or nanoscale [1].

In the following subsections I will summarize the results obtained in the experiments aimed to produce color center containing diamond nanostructures, namely nanocrystalline diamond films, individual nanocrystals and nanopillars.

a) Nanocrystalline diamond films

Series of nanocrystalline diamond thin films containing SiV centers with different morphologies were successfully deposited on one-side polished silicon substrate by MWCVD technique. Si wafer played the role of a substrate for the diamond films and the impurity source for doping the growing nanocrystals, as well. The morphology of the prepared samples was controlled by the deposition parameters, particularly by the methane content of the source gas and by the substrate temperature, applied during the growth process. While the former was varied between 0.2 and 3%, the latter was increased from 650 to 850 ^{o}C with 50 ^{o}C steps [2].

It was found that with increasing methane content the morphology of the obtained films gradually transforms from nanocrystals with well-defined facets and crystal shape to a cauliflower-like structure built up of tiny crystals of nearly spherical shape (see Fig. 1). The reason behind this is the increased concentration of the carbon radicals in the source gas, which are the building units for the growing diamond structure, that leads to renucleation on the growing surface and blocks the growth of dominant crystal planes [5].

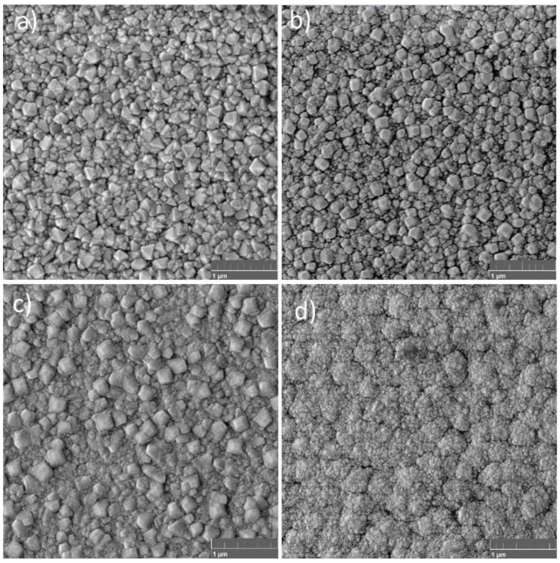

Figure 1: The surface morphology of nanocrystalline diamond thin films deposited at 750 ^{o}C substrate temperature and varying methane content in the source gas: a) 0.2%; b) 1%; c) 1.5%; d) 3%.

In the case of the substrate temperature, its impact on the morphology of created nanodiamond thin films is not as evident as for the methane content. However, in general we found that a higher temperature leads to a larger average crystal size but, based on our experimental results, this linear dependence is interrupted at a very high substrate temperature (~750 ^{o}C), above which the graphitic content of the deposited nanodiamond structures increases rapidly. It was explained by the changes in the reaction kinetics, observed at the highest substrate temperature used in our experiments, at which the plasma conditions are more favorable for the formation of sp^2 carbon structures, which cannot be efficiently suppressed anymore by the hydrogen ions (etching process) at given methane/hydrogen input source gas ratio.

Our experimental results demonstrate that by varying the source gas ratio and substrate temperature during the MWCVD process, the morphology of created nanodiamond thin films can be tuned from the well-determined faceted crystal shape to the cauliflower-like structure. Parallel to this, we can keep the condition for the incorporation of Si impurity atoms and forming SiV centers with sufficient efficiency. However, the morphology plays an important role in the SiV emission properties as it will be discussed later.

b) Individual diamond nanocrystals

As a next step, we started experiments the aim of which was to produce color center containing individual diamond nanocrystals to limit dimensions in the space for diamond-based quantum emitters. Two approaches were used. In one type of experiment Si impurity-free monodispersed detonation nanodiamonds (DND) of 10 nm in diameter suspended in water were spin-coated on a Si substrate and after drying it was placed into the MWCVD reactor for a normal diamond growth process. In the second case, we used a special bias enhanced nucleation as a first step of the CVD growth. Conditions for the low concentration seeding, at which the diamond nuclei are enough far from each other to eliminate the formation of a layer, were determined experimentally. During these experiments we found out that bias enhanced nucleation is much more beneficial compared to the DND-based seeding. First, it allows to control the size of the growing nanocrystals, as well as their distribution on the substrate (for overgrown DND crystals we usually observed agglomeration of nanodiamonds and appearance of small islands after the overgrowth process (see Fig. 2)). Second, the intensity of the SiV color centers was usually higher in bias-enhanced samples, especially of smaller size. This was explained by the smaller volume available for the incorporation of Si impurity in case of the DND seeded samples, since they do not contain silicon impurity. In contrast, the bias enhanced nucleation allows the incorporation of impurities from the very beginning of the growth process [3].

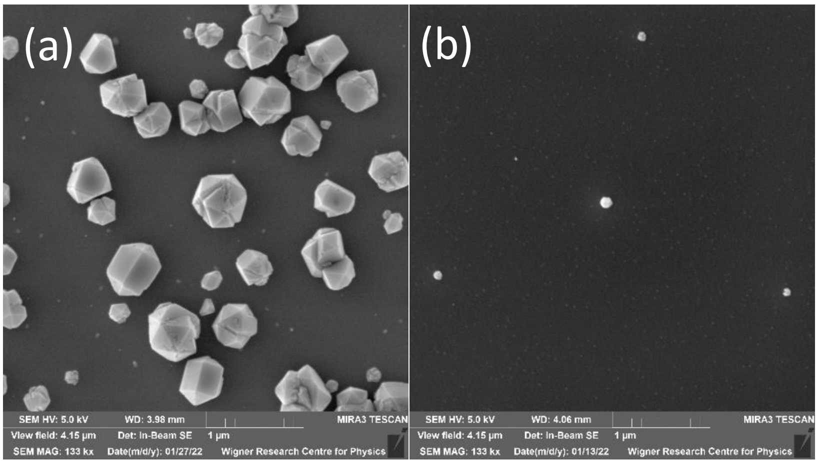

Figure 2: SEM images of the SiV center containing individual diamond nanocrystals obtained by overgrowing (a) DND diamond seeds and (b) bias enhanced nuclei.

c) Diamond nanopillars

Diamond nanopillars of different sizes were fabricated from a ~1.2 μm thick nanocrystalline diamond thin film by combining the conventional electron beam lithography and reactive ion etching (RIE) process and by FIB milling in cooperation by the Kassel University and HUN-

REN Centre for Energy Research, respectively. The initial nanodiamond thin film was grown in our home-built MWCVD setup using an electric grade pure, one-side polished Si wafer as a substrate which served simultaneously as a Si impurity source for SiV centers. To prevent collective effects and enable the investigation of individual pillars, the distance between the centers of neighboring pillars was set to 5 µm. The produced pillars, based on their diameter and height, can be divided into two groups: pillars with constant height (h) and pillars with constant radius (r). Pillars with constant height (same as for the initial film, h=1200 nm) and distinct radiuses of 500, 300, and 200 nm belong to the first group, while pillars with constant radius (r=200 nm) and three different heights of 1200, 600, and 300 nm belong to the second group.

Contrary to our expectations, these experiments showed that the FIB milling has more disadvantages for the creation of diamond nanostructures containing color centers compared to the chemical method. The used Ga ions destroyed the diamond crystalline structure during the milling process and was not possible to completely restore it even after multistep heat treatments as we have seen in our previous works. Additionally, the control of the required size of the nanoobjects is much more challenging then for the chemical method. The shape of the pillars we obtained by the FIB milling was more spherical-like compared to the RIE technique, which is a serious disadvantage if the height to radius ratio is important (see Fig. 3).

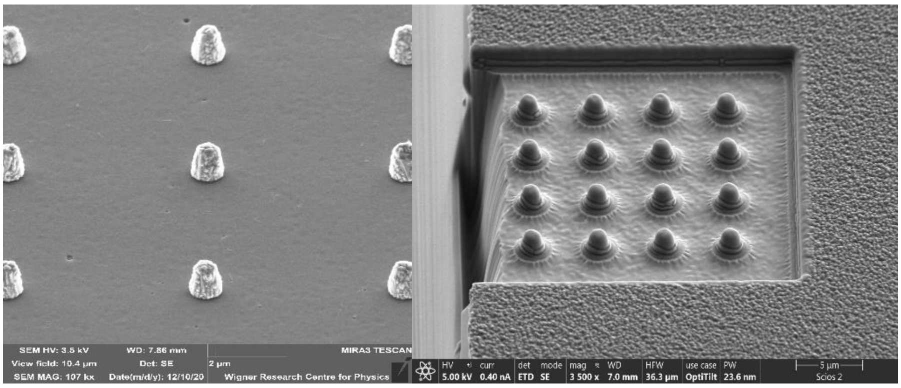

Figure 3: SEM images of nanopillars with height of h=1200 nm and radius r=500 nm prepared by (a) the combination of electron beam lithography and reactive ion etching and (b) FIB milling.

2. Investigation of SiV and GeV center containing diamond nanostructures

The properties of the produced color center containing diamond nanostructures, described in the previous part, were studied by different methods. The morphology and size of the nanostructures were investigated by scanning electron microscopy. The quality of the structures and phase identification, as well as the defect and impurity analysis, were done using Raman spectroscopy, high-resolution TEM, and XPS analysis. Light emission and scattering properties were investigated by photoluminescence and dark-field micro-spectroscopy. The obtained results are discussed in the following subparts.

a) Morphology dependent emission properties of the SiV and GeV centers in nanocrystalline thin films

Emission properties of the silicon and germanium related defects in nanocrystalline diamond thin films were studied systematically. It was shown that the morphology of the films strongly influences the emission intensity as well as the peak position and full width at half maximum (FWHM) of the zero-phonon line (ZPL). Interestingly, increasing the CH_4 concentration in the source gas from 0.2% to 1.5% increased spectacularly the ZPL intensities for both types of color centers, but the further increase of the CH_4 concentration to 3% caused a rapid drop down in them (see Fig. 4). This was explained by two factors. First, the growth rate at higher methane concentrations is significantly increased and the time available to establish chemical bonds for Si or Ge radical with the carbon atoms and to form stable defects on the growing diamond surfaces is decreased. Secondly, the ratio of locally available impurity atoms and carbon radicals exceeds the point where the probability of impurity incorporation is much lower than the renucleation of new diamond seeds on the growing surface. The appearance of a cauliflower-like structure at the highest CH_4 concentrations (see Fig. 1) observed in our experiments is in good correlation with the latter interpretation.

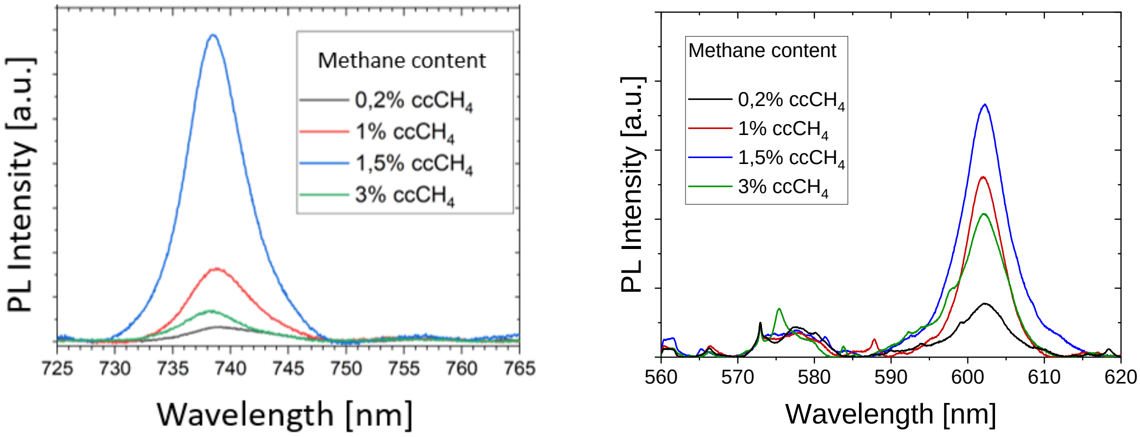

Figure 4:Photoluminescence spectra of (a) SiV and (b) GeV color centers in nanocrystalline diamond having different morphologies (see Fig. 1).

The peak position and FWHM of the color center ZPLs were also investigated, since these parameters determine the indistinguishability and noise of a quantum emitter. We found that the zero-phonon line (ZPL) peak position is less sensitive to the morphology. However, in the case of individual nanocrystals the spread of the peak position can exceed 5 nm for SiV and 10 nm for GeV containing samples. In contrast, the ZPL width varies over a relatively broad range. The difference between the narrowest and widest ZPLs obtained on our samples can reach one order of magnitude at room temperature and it is more spectacular for SiV centers. These significant differences in FWHM values were ascribed to the varying local stress that acts on individual color centers and it is more expressed for samples characterized by broad nanocrystal size distribution. Nevertheless, the most spectacular impact caused by the varying morphology/deposition parameters observed for the SiV center peak intensity. We found that the temperature of the silicon wafer, used as an impurity source during the CVD diamond growth process, is critical in terms of SiV center formation efficiency. Based on these findings, we have developed a new and more efficient technique for the creation of high-quality CVD diamond nanostructures with bright and stable SiV emission. The new technique is based on a plasma immersion method and utilizes the increased contact surface between the impurity source and the CVD plasma. Due to the increased temperature and beneficial geometry for the silicon etching, the number of incorporated SiV centers dramatically increases. Our results show that the SiV center's emission peak intensity for the nanodiamond sample prepared by the newly developed technique is almost 10 times higher than that of the configuration without the additional Si source. Additionally, TEM and SEM investigations confirmed that the obtained structure is a polycrystalline diamond, in which the diameter of nanocrystals ranges between 20-50 nm. XPS studies proved that the sp^2 carbon content of the structure is less than few percent and the Si impurity level is 0.02 at.% [10].

In case of the GeV centers the changes are even more spectacular. Obtaining nanocrystalline diamond films with intense and homogenously distributed GeV centers was possible only with the newly developed doping geometry [3]. We should note that the formation of GeV centers was possible to realize by using impurity sources with larger area than for the SiV ones and the process was accompanied by the appearance of germanium nanocrystals, implying on the lower probability of incorporation of Ge atoms than Si.

b) Light emission properties of the SiV and GeV centers in individual nanocrystals

In the case of nanocrystals, the formation of GeV centers is much more difficult as it was demonstrated in our experiments, even by newly developed geometry, especially for the size range (≥ 50 nm) interesting for us.

Neither the XPS investigation nor the secondary neutral-particle/ion mass spectroscopic analysis were able to detect Ge impurity-related signals. Photoluminescence investigation showed that in some crystals the GeV center related ZPL at ~602 nm can be detected when scanning a large area, but it appears orders of magnitude less frequently than the SiV center related ZPL at ~738 nm. We explained it with the limitation of the volume in which the internal strain caused by the Ge impurity atoms having a larger radius than Si, cannot be tolerated by the crystal field without collapsing the diamond structure at this size range [8].

In contrast to GeV centers, the SiV center formation in individual diamond nanocrystals does not show any discrepancy. However, the intensity distribution of the ZPLs is much broader than in the case of thin films. It was found by investigation of the long-term intensity stability of SiV center containing fluorescent nanodiamonds, that nanocrystals can be divided into two groups: crystals with moderate and nearly constant SiV peak intensity and nanodiamonds with high but slightly decreasing in time PL intensity (see Fig. 5) [10].

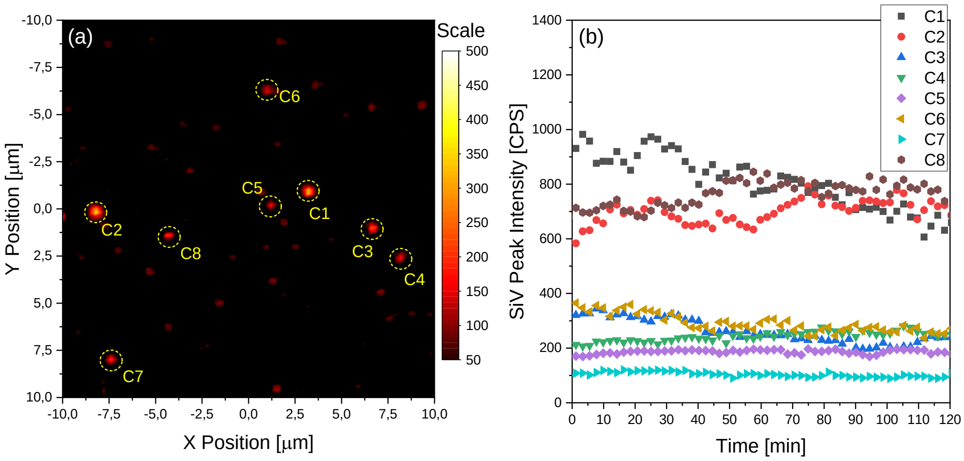

Figure 5: (a) Confocal PL map of a randomly selected area (20x20 µm^2) of the SiV center containing individual nanocrystals (b) the long term intensity stability data of fluorescent nanodiamonds randomly selected from the mapped area.

c) Photoluminescence studies of color center containing nanocrystalline diamond pillars

Light emission properties of the SiV center containing diamond nanopillars obtained by two different methods (electron beam lithography + RIE and FIB milling) were investigated to determine the effect of the structuring on the emission properties. We found that in the case of the FIB milling the applied Ga ions destroyed the crystalline structure and caused a serious graphitization of the diamond. This was supported by the multiwavelength Raman excitation measurements also. Additionally, it was concluded that besides the sp^2 carbon phase the number of interstitial carbon atoms is also increased as a result of FIB milling. To restore the crystalline structure, the samples were annealed in a vacuum furnace at 800 °C for 2 hours. It was followed by an oxidation treatment at 400 °C by placing the samples into a constant air flow. Despite of the applied complex heat treatments the crystallinity of diamond nanopillars was not completely recovered and PL intensity of the SiV center peak was lower than in the initial film. Due to the experimentally observed disadvantages, these samples were not further investigated.

For pillars obtained by the combination of electron beam lithography and RIE, the picture is completely different. During a systematic study, it was discovered that nanodiamond pillars can enhance the intensity of both, the photoluminescence and Raman-scattering signals. Detailed results will be presented in the following section.

3. Enhancement of the light emission properties of the color centers embedded into different diamond nanostructures

One of the most important requirements for a quantum emitter is to have a bright and stable emission signal. Since the emission intensity of color center containing diamond nanostructures are not completely satisfactory, one of the aim of this project was to enhance the photoluminescence signal related to the SiV and GeV color centers. We used different approaches to enhance the signal intensities coming from the fluorescent nanodiamonds. One of them was to increase the efficiency of the incorporation and color center formation process during the growth of nanodiamond structure. This was achieved by the new doping geometry that was developed during the project and demonstrated for nanocrystalline diamond thin films and individual nanocrystals. The efficiency of the technique in the case of SiV center containing individual nanodiamonds can exceed one order of magnitude [10].

Second approach was discovered during the systematic studies of color center containing polycrystalline diamond nanopillars. We found that depending on the dimensions of nanopillars and applied laser excitation, the photoluminescence signal of the embedded SiV centers can be significantly enhanced. Two possible explanations were proposed: a) diamond nanopillars act as solid immersion lenses and allow more efficient collection of the incoming excitation photons and direct emitted ones to the objective and detector system; b) nanopillars act as resonant nanoantennas and at special conditions, they can trap the incoming photons which are bouncing within the nanostructures back and forth resulting in multiple light-matter interactions. The highest enhancement factor, relative to the initial thin films, we obtained on our nanopillars was 20 for SiV center [12].

This phenomenon was modelled by using Lumerical and COMSOL Multiphysics software packages. A simplified model of the diamond nanopillars of h=1200 nm height and different radiuses were surrounded by air and the plane wave excitation was applied in the direction perpendicular to the top surface of the pillar. Wavelength dependent studies showed that internal hotspots appear at different places and far-field scattering patterns show resonances at special wavelengths. These special wavelengths are usually close to the laser wavelength at which the highest photoluminescence enhancement was observed. The differences can be explained by the polycrystalline character of the diamond pillars and their rough surface which is not taken into account in the model [11].

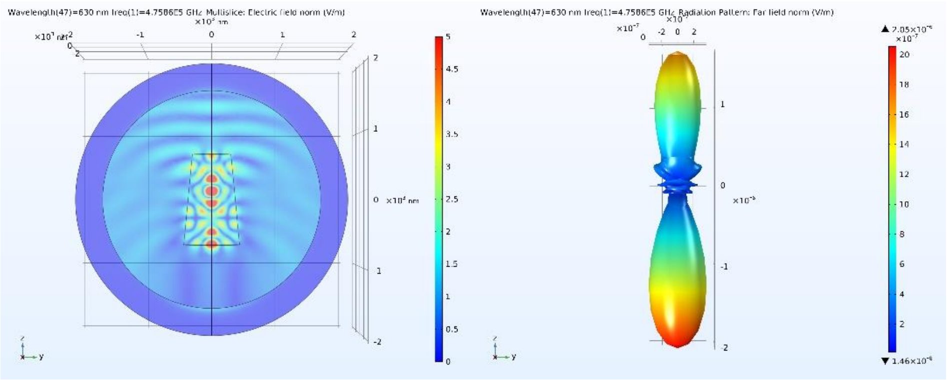

Figure 6: The calculated intensity distribution of electromagnetic field and far-field scattering pattern for diamond nanopillar with height of h=1200 nm and top and bottom radii of 300 and 500 nm, respectively.

To extend our studies on the photoluminescence behavior of color center containing diamond nanostructures we prepared a sample series with very exotic surface morphology. SiV center containing nanodiamond films with nanocrystals of pyramidal, truncated pyramidal, randomly oriented and cauliflower-like shapes were produced. We found that the SiV photoluminescence signal on truncated pyramids is spectacularly higher than in other places or types of samples. Within the framework of these experiments, we were able to enhance the PL signal by exotic surface morphology that was obtained by using special growth conditions, without applying a difficult and time-consuming structuring process. The intensity enhancement at truncated pyramids relative to the randomly oriented crystals exceeds 100 (see Fig. 7) [6].

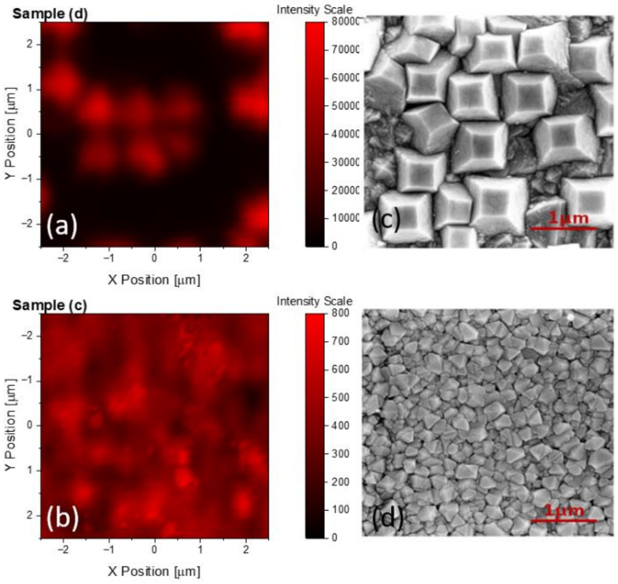

Figure 7: Photoluminescence intensity distribution of SiV centers (in (a) – truncated pyramidal, (b) – randomly oriented nanodiamond samples) and SEM images of the surface morphologies for (c) truncated pyramidal and (d) randomly oriented samples, respectively.

Applying gold nanospheres and rods as plasmonic nanostructures was the third approach for the signal enhancement of fluorescent diamond nanostructures we prepared by MWCVD. Experiments were performed by gold nanospheres of 20 nm in diameter prepared in our laboratory [9]. After dropping and drying out these nanospheres on the top of color center containing diamond nanocrystals, photoluminescence and Raman measurements were performed with different wavelengths [7]. A weak signal enhancement was observed at some places, where nanospheres are accumulated, but the efficiency was far from the approaches described above. This can be attributed to the plasmon resonance frequency which is far from the SiV center PL band, or to the large distance between the nanospheres and color centers which prevents sensing the plasmonic field.

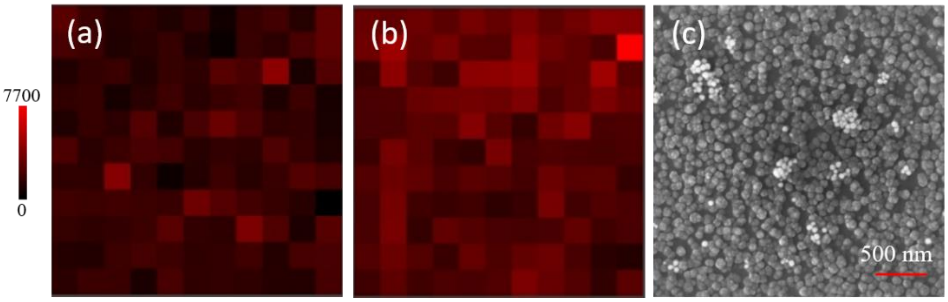

Figure 8: PL maps of SiV center signal (a) without and (b) with gold nanospheres. (c) SEM image of the diamond sample with gold nanospheres on the surface.

Summary

Despite the difficulties, the main goals determined in the proposal were achieved and SiV and GeV center containing diamond nanostructures of different forms were successfully prepared and studied in detail by different methods. The light emission properties of color center containing diamond nanostructures were systematically investigated. A strong influence of the morphology on the light emission properties being relevant for quantum light source application was revealed and analyzed. The photoluminescence signal of these color center containing nanodiamond structures was enhanced significantly by using several approaches. The results were published in two peer-reviewed journal papers, and there is one submitted and one “in preparation” manuscript. A book chapter on the topic of this research was published in Hungarian. Additionally, the obtained results were presented at national and international conferences as oral and poster presentations. One BSc thesis was successfully defended under my supervision.

During the realization of this OTKA project, several unforeseen difficulties appeared. The forced break due to the COVID-19 pandemics, followed by the energy crises caused troubles in the heating of laboratories, slowing down the experiments. This also led to the termination of my student’s contract, and technical difficulties with our home-built MWCVD system related to the power supply and later to the sample heating control unit. All these factors made the research very difficult.

I would like to thank the NKFIH-OTKA committee for approving my extension request to complete the final professional report.

References

1) L. Himics: *Gyémánt: csillogó drágakő a jövő technológiáiban, avagy egy kristály élete az ékszeriparon kívül,* Terítéken a tudomány Természettudományt mindenkinek! Ungvár 2021 - book chapter
2) Bodoky Lukács Márk: *Nanogyémánt vékonyrétegek, mint színcentrum mátrixanyagok tulajdonságainak vizsgálata*, BME Természettudományi Kar, 2022 – BSc thesis under my supervision
3) L. Himics, D. Gál, P. Csíkvári, R. Holomb, I. Rigó, A. Jaafar, T. Váczi, M. Veres: *Incorporation and photoluminescence properties of GeV centers into CVD nanocrystalline diamond films,* Budapest School on Modern X-ray Science 2023 – poster presentation
4) L. Himics, D. Gál, P. Csikvári, R. Holomb, I. Rigó, T. Váczi and M. Veres: *Formation efficiency and photoluminescence properties of SiV- centers in CVD nanocrystalline diamond structures with different textures,* 33rd International Conference on Diamond and Carbon Materials, Mallorca, Spain 2023 - poster presentation
5) M. Veres, I. Rigó, T. Váczi, R. Holomb, V. Ralchenko, C. Popov, L. Himics: *Incorporation of nitrogen into nanocrystalline diamond films studied by multi-wavelength Raman spectroscopy,* 33rd International Conference on Diamond and Carbon Materials, Mallorca, Spain 2023 - poster presentation

6) L. Himics, D. Gál, P. Csikvári, R. Holomb, T. Váczi, Margit Koós and M. Veres: *Surface morphology dependent emission properties of colour centre containing CVD nanodiamond films*, SBDD XXVIII 2024, Hasselt, Belgium - poster presentation
7) M. Veres, I. Rigó, T. Váczi, R. Holomb, V. Ralchenko, C. Popov, L. Himics: *Study of the incorporation of impurity atoms into nanocrystalline diamond films by multi-wavelength Raman spectroscopy,* SBDD XXVIII 2024, Hasselt, Belgium - poster presentation
8) L. Himics, D. Gál, P. Csíkvári, M. Veres: *Preparation and characterization of nanocrystalline diamond films and particles incorporating metalloid-related colour centres* Wigner 121 Scientific Symposium 2023, Budapest, Hungary – poster presentation
9) L. Mikac, I. Rigó, L. Himics, A. Tolić, M. Ivanda, M. Veres: *Surface-enhanced Raman spectroscopy for the detection of microplastics*, Applied Surface Science 608: 155239, 2023 – article
10) L. Himics, D. Gál, P. Csíkvári, R. Holomb, M. Koós, A. Sulyok, B. Pécz, M. Veres: *A modified plasma immersed solid-phase impurity assisted doping geometry for the creation of highly fluorescent CVD nanodiamond,* Vacuum (216) 112493, 2023 – article
11) Himics L., Gál D., Csíkvári P., Holomb R., Váczi T., Veres M.: *Ponthibákat tartalmazó gyémánt nanoszerkezetek előállítása és spektroszkópiai vizsgálata*, XV. Környezetvédelmi Analitikai és Technológiai Konferencia és 63. Magyar Spektrokémiai Vándorgyűlés, Balatonszárszó, Hungary 2024 – oral presentation
12) L. Himics, N. Felgen, C. Popov, A. Deák, D. Gál, P. Csíkvári, R. Holomb, M. Veres: *Raman and photoluminescence signal enhancement by nanocrystalline CVD diamond pillars*, Diamond and Related Materials, submitted article