Summary of the Ph.D. thesis

Creation and spectral characterization of luminescence centers in nanodiamond

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1. Introduction

Optically active defect centers in nanodiamond crystals generate a distinct research interest in the last decade. The challenge for creation of extremely high quality nanodiamond structures in a few nanometer size scale and the introduction of individual color centers into them is still open. This high interest towards color centers is initiated by their unique physical and optical properties like intensive, stable and narrow emission band, lack of blinking or bleaching even at room temperature, single photon emission and optically addressing and readout of the spin state as well. These properties of color centers in combination with the extreme nature of diamond as host material allow to develop new devices in the field of the quantum information processing, nanophotonics, nanobiology and nanomedicine.

The applications in nanobiology or nanomedicine are based on the biocompatibility of the nanodiamond crystals with color centers: In contrast to the nanotubes, the introduction of nanodiamonds into living systems as "*in vivo*" imaging or labeling tools has no risks of cancer formation. For many other applications, however, most important properties of color centers in nanodiamond crystals are those, that could help to resolve problems in quantum computing and quantum cryptography. These will help to construct quantum computers, one of the biggest scientific challenges in the 21st century. One main constituent of quantum computers is the so called Quantum Information Processing (QIP) unit that is based on quantum mechanics and contains several practical applications. Criteria of the construction of quantum devices are the effective creation and manipulation of single quantum states within nanometer size with high precision. Since the quantum state of the light – the photon – fulfills these criteria, moreover

it enables the transmission of information with speed of light over long distance without high noise and coherency loss, thus the diamond crystal containing color center can be used as building block of QIP systems. Single photons can easily be used as quantum bits (qubit), where the information is encoded into the polarization state of individual qubits. In order to realize qubits it is necessary to create reliable and perfect single photon emitters that absolutely photostable (no blinking or bleaching), emit only one photon per one excitation pulse and whose emitted photons are indistinguishable. These conditions can be fulfilled mainly by quantum dots and by color centers in diamond. Most important benefits of latter are the high photostability and higher working temperature range and also the relatively simple creation process.

The main objectives of my research work were the creation and spectral characterization of different color centers in nanodiamond structures, which have excellent properties for the applications mentioned previously or offer alternatives for the existing ones.

The first part of my dissertation details the creation of complex nitrogen-vacancy defect, the so called N3 center, created posteriorly in detonation nanodiamond crystals by using different ion implantation techniques. The center consists of a carbon vacancy surrounded by three neighbor nitrogen atoms and its zero-phonon line (ZPL) is located in the deep blue wavelength region at 2.985 eV (415 nm). In addition to the excellent luminescence properties the N3 center is paramagnetic, that allows using it for quantum information processing.

The natural diamond crystals often contain N3 centers, but their posterior formation in nanodiamond structures was not resolved yet. In our experiments we created N3 color centers in detonation nanodiamonds

having 12 nm average crystal size using different ion implantation techniques at moderate ion energies and ion fluxes combined with complex heat treatments. The successful creation of the N3 center was confirmed by photoluminescence emission and excitation spectroscopy and by detailed analysis of the ZPL and its phonon sideband fine structure. The changes in bonding configuration of the diamond structure caused by ion implantations and different heat treatments were monitored by Raman spectroscopy.

The second part of the dissertation deals with the results obtained during the detailed study of the ZPL emitted by silicon-vacancy (SiV) centers created in nanodiamond thin films at different conditions. The relationship between the changes of the ZPL spectral parameters and the residual stress determined from the diamond Raman peak measured in the vicinity of SiV centers is discussed. Connection was also found between the average grain size of the nanodiamond films and the spectral parameters of the SiV centers ZPL. This can be explained by the formation of a phononic bandgap due to crystal size, that suppresses the propagation of phonons of specific frequency. An important result is the increasing concentration of emission intensity into the SiV centers ZPL as the compressive residual stress of nanodiamond films increases. The internal residual stresses were determined from the diamond peak in Raman spectra recorded form the same sample volume as the luminescence spectra. The average grain sizes were determined by analyzing the scanning electron microscopy (SEM) pictures.

The SiV center is a preferred candidate as single photon emitter. The ZPL of SiV center is located at 1.681 eV (738 nm) that is in the highest optical transmission window of live tissues. Moreover, the center has low electron-phonon coupling, therefore the luminescence intensity is

concentrated mainly into the ZPL. Thus the SiV centers preferred for quantum information processing and biological applications at the same time.

2. Scientific background and goals

The unique properties of nanodiamond structures containing different color centers can bring a breakthrough in different research and application fields like quantum computing and cryptography, or can revolutionize areas like nanobiology and nanomedicine. There are more than 500 optically active defects in diamond, but only a small part of them, having extreme physical properties, can be used in real applications. The main part of previous studies was focused on the nitrogen related optical defects, especially on the nitrogen-vacancy center, that exist in two charge states. For quantum computing application the negatively charged nitrogen-vacancy (NV^-) center is preferred, but the high electron-phonon coupling of the center limits the practical application potential. As a result, creation of new color centers with physical and optical properties similar or better than the NV^- is required. In many aspects the N3 defect, consisting of a carbon vacancy surrounded by tree neighbor nitrogen atoms, and well known in bulk diamond crystals, is a good candidate. In addition to the paramagnetic properties, the ZPL of N3 center is located at 2.985 eV that is also preferable for many applications and allows to construct solid state lasers emitting in the deep blue wavelength region. Despite of the fact that numerous color centers studied in bulk diamond crystals were also created in nanodiamond structures and that the nitrogen easily incorporates into the diamond structure, the posterior creation of N3 centers in nanodiamond structure was not resolved yet. The applied high ion energy and doses used for bulk

crystals are not completely suitable for implantation of nanodiamonds, due to large structural damages caused by the high energies and fluxes. Thus, the implantation parameters and methods used earlier have to be revised and new technological processes specific for nanodiamond structures have to be developed.

Beside the nitrogen related color centers the silicon-vacancy center has similar or even better unique properties. Thus a detailed study of their properties is highly preferred. This center consists of a carbon vacancy and a silicon atom in a so called split vacancy configuration. The SiV center is a single photon emitter and has very low electro-phonon coupling, moreover its ZPL is located in the near-infrared wavelength region. This makes it preferred not only for quantum computing, but for biomedical applications also. The ZPL of SiV center is located around 1.681 eV, but it can shift a few meV, depending on the sample, which restricts the indistinguishable single photon emission, being essential for quantum computing applications. The full width at half maximum of the ZPL is also varies and this limits the information transmission by photons.

Goals of my research work:

- Creation of nitrogen related complex defect structure in nanodiamond crystals with average grain size below 20 nm, by using simple and widely spread techniques that minimalize the damage of the host material. The complex defect should have useful properties for practical applications.
- Development of complex heat treatment procedures for effective creation of complex defects and for relaxation of implanted crystal structure. Monitoring of these changes by Raman measurements. Identification of created defects by luminescence investigations and detailed analysis of the ZPL and phonon sideband fine structure.

- Creation of silicon-vacancy centers in nanodiamond films deposited at different growth conditions for subsequent study of the changes in SiV ZPL spectral parameters.
- Determination of the spectral parameters of SiV centers ZPL by photoluminescence spectroscopy. Evaluation of the changes in spectral parameters as a function of residual internal stress and average grain size of the nanodiamond film host.

3. Sample preparation and investigation methods

High quality detonation nanodiamond crystals (NEOMOND Ltd) in powder form were used for the creation of N3 centers. According to the product datasheet the powder contains nanodiamond crystals with sizes from 3 to 20 nm. This was confirmed by our measurements also. A 3 hours long ultrasonic treatment was used to create nanodiamond slurry with concentration of 1.5 mg/ml. Thin films were formed from this slurry by dripping it onto silicon wafer and drying for 48 hours.

The nitrogen-vacancy complexes were created posteriorly using different ion implantation techniques at the Institute of Materials and Environmental Chemistry of HAS. For the first carbon vacancies were created by He^+ bombardment, which was followed by N_2^+ ion implantation to introduce significant amount of nitrogen impurities into the structure.

The ion implantation was performed using two different implantation techniques: plasma immersion ion implantation (PIII) and focused ion beam (FIB) treatment. In the case of PIII 30 and 20 keV ion energies were used, while the ion flux was between 10^{15}-10^{17} ion/cm^2. The FIB implantations were performed at 2 keV ion energy and 10^{15} ion/cm^2 ion flux via raster scanning of the sample.

The depth distributions of created vacancies and implanted nitrogen ions were determined by SRIM (Stopping and Range of Ions in Matter) calculations for all implantation parameters.

Ion implantation was followed by a two step complex heat treatment in all cases. First, nanodiamond "films" were heat treated for 2.5 hours in high vacuum (3.5×10^{-5} mbar) at 750 ^{o}C with the aim to initiate vacancy migration and decrease the stress in the structure caused by ion implantation. It was followed by an oxidation process at 450 ^{o}C in air for 5 hours to decrease of the sp^2 bonded carbon content formed on the surface of crystals during the ion implantation.

The optically active defects created by ion implantation and subsequent complex heat treatment were studied by photoluminescence spectroscopy, while the changes of the bonding configuration were investigated by Raman spectroscopy.

Luminescence measurements were performed on a Horiba Jobin Yvon FL3-221 spectrofluorimeter. The photoluminescence emission (PL) spectra were recorded in the 1.65-4.25 eV (750-290 nm) photon energy region at different excitation energies. A 450 W Xe arc lamp was used as excitation source. The photoluminescence excitation (PLE) spectra were taken by the same spectrofluorimeter in the 4.959-1.378 eV photon energy region. Both, the PL and PLE spectra were investigated at cryogenic and elevated temperatures. An Air Product closed cycle cryostat was used for the cooling of the sample with helium coolant medium.

Raman spectra were recorded on a Renishaw 1000 Raman spectrometer equipped with Leica DM/LM microscope in the 800-2000 cm^{-1} wavenumber region with ~1 cm^{-1} spectral resolution. The excitation source was a 488 nm laser line of a Spectra-Physics Ar ion laser. The laser spot was

focused into a spot of ~1 micron in diameter using objective lens with 100x magnification.

The SiV centers were formed during the nanodiamond film growth in our laboratory using microwave enhanced chemical vapor deposition (MW CVD) method. During the deposition process the CH_4 concentration of the feed gas mixture and the substrate temperature were changed in order to create SiV centers in nanodiamond thin films of different morphology and texture. An additional piece of silicon wafer was placed in the plasma chamber to have a continuous Si impurity supply in the plasma. The power of microwave generator was 1200 W during the deposition process. The CH_4 concentration in the source gas mixture was changed from 0.2 to 3.0%, while the substrate temperature was ranging from 650 to 850 ^{o}C. The deposition time for each case was limited to 2 hours.

The bonding of nanodiamond films with SiV defect center was monitored by Raman spectroscopy. The ZPL parameters of SiV centers were determined from the luminescence spectra by fitting procedure. Both luminescence and Raman spectra were recorded simultaneously from the same sample volume in the Raman microscope, which allowed to study relationship between changes in ZPL spectral parameters and residual internal stress in the surrounding of the SiV centers. The residual internal stresses were determined from analysis of the diamond peak in Raman spectra. Both, the photoluminescence and Raman spectra were recorded by previously mentioned Renishaw 1000 micro-Raman spectrometer. In most cases the 488 laser line of an Ar ion laser was used as excitation source, but luminescence measurements were performed by using different laser diodes [405 nm (3.06 eV), 532 nm (2.33 eV) and 635 nm (1.95 eV)]. The spectral

resolution of the measurement system at SiV center peak position was 0.25 meV.

The texture of the SiV containing nanodiamond films was investigated by scanning electron microscopy. The SEM pictures were obtained on a Leo 1540XB workstation at different magnifications. The SEM pictures were used to determine the average grain size of the films. SEM investigation were made at the Institute of Technical Physics and Materials Science of HAS.

4. New scientific results

The new scientific results achieved in my research work are summarized in the following Thesis:

1. I showed experimentally that color centers emitting intensively even at room temperature in the deep blue wavelength region can be created in nanodiamond crystallites of 12-20 nm average grain size by the implantation of N_2^+ and He^+ ions at moderate ion energies (2-30 keV) and ion doses (1.5-4.5×10^{15} ions/cm^2) using relatively simple and widely available plasma immersion ion implantation (PIII) or focused ion beam (FIB) techniques and subsequent complex heat treatments. The implantation depth of N_2^+ and He^+ ions and the distribution of the created lattice defects were determined using the SRIM simulation program. [T1]

2. By the detailed investigation of the photoluminescence spectra of implanted nanodiamonds I showed that the intensive and narrow emission band detected in the deep blue wavelength region is related to a complex nitrogen-vacancy defect structure, the so called N3 center. This was confirmed by the shape of the emission band and the position of the zero phonon line (~2.985 eV) determined by fitting. The significant ZPL

broadening (of 68-75 meV) observed in our samples is related to the inhomogeneous line broadening mechanism, caused by the differently relaxed local environment of the N3 centers. [T1, T2]

3. By the investigation of the phonon sideband structures in the photoluminescence spectra recorded at 8 K I showed that the created complex defect center contains a vacancy fragment and the position of fine structures are in good agreement with the vibrational energies of phonon structures characteristic for the N3 center created in bulk diamond. The maximum of luminescence excitation spectrum recorded at 8 K is located at 3.37 eV, which is typical for N3 center. The local maximum at 3.66 eV was assigned to the so called N4 optical transition related to the same N3 defect structure. [T2]

4. By mapping the spectral parameters of the SiV ZPL within a 10×10 μm^2 area on nanodiamond thin films I showed that the SiV centers have only slightly different environment. The deviation of the spectral parameters does not exceed 0.8 meV for a sample deposited at given conditions. Using multiwavelength laser excitation I showed that the asymmetric line shape of the SiV centers formed at different conditions is caused by the emission of the GR1 center. By scanning photoluminescence measurements I showed that the emission of the GR1 center is well distinguishable from the emission of the SiV center in areas with high local concentration of the GR1 centers. [P1]

5. By using different preparation conditions SiV centers of different local surroundings were formed in nanodiamond thin films. The residual internal stress in the local vicinity of SiV centers, determined from the diamond Raman peak was used to characterize the local surrounding of the

SiV centers. I showed that the spectral parameters of the zero phonon line of the SiV center depend on the internal stress. The ZPL peak position was found to be blue-shifted by 2.6 meV and narrowed from 18.1 meV to 6.4 meV when the tensile internal stress of 0.64 GPa changes to compressive stress of 2.25 GPa. The dependence of the ZPL spectral parameters on the local internal stress can be explained by the higher splitting of both the ground and excited states of the electronic levels of the SiV center due to the increased local internal stress, which suppresses the rate of the orbital relaxation via low energy acoustic phonons. [T3, T4]

6. I showed that the ZPL spectral parameters of SiV centers created under different conditions depend on the average grain size used to characterize the texture of the nanodiamond films. The ZPL peak position shifts to higher values and the peak narrows when the average grain size decreases from 150 nm to 30 nm. This tendency can be related to phononic band gap being dependent on the size of the nanodiamond grains, which restricts the propagation of acoustic phonons and so the relaxation processes following the photoexcitation. The confinement causes the formation of a total phononic band gap in grains having size below 120 nm for the acoustic phonons with <50 GHz frequency. [T4]

5. Publications

Publications related to the thesis:

[T1] **Himics L.**, Tóth S., Veres M., Tóth, A. and Koós M. (2015). Effective implantation of light emitting centers by plasma immersion

ion implantation and focused ion beam methods into nanosized diamond, Applied Surface Science 328, 577.

[T2] **Himics L.**, Tóth S., Veres M., Balogh Z. and Koós M. (2014). Creation of deep blue light emitting nitrogen-vacancy center in nanosized diamond, Applied Physics Letters, 104(9), 093101-01.

[T3] **Himics L.**, Tóth S., Veres M., Csíkvári P. and Koós M. (2015). Influence of microwave plasma parameters on light emission from SiV color centers in nanocrystalline diamond films, Open Chemistry, 13(1), 263.

[T4] **Himics L.**, Tóth S., Veres M. and Koós M. (2016). Spectral properties of the zero-phonon line from ensemble of silicon-vacancy center in nanodiamond, Optical and Quantum Electronics 48(8), 394.

[P1] **Himics L.**, Tóth S., Veres M., Rigó I. and Koós M. (2016). Investigation of the 1.68eV Near-Infrared Emission Lineshape in Nanodiamond Films by Selective Laser Excitation, International Conference on Advanced Laser Technologies (ALT) 2016, 2016. szeptember 12-16., Galway, Írország (poster).

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2. Tóth S., **Himics L.** and Koós M. (2015). Nickel-Silicon Related Color Center Formed in Nanodiamond Grains under CVD Growth, Journal of Nanoscience 2016, 282967.
3. Tóth S., **Himics L.**, Veres M., Balogh Z., Ralchenko V. G. and Koós M. (2015). Zero-phonon line characteristics of SiV center emission

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4. **Himics L.**, Tóth S., Veres M., Czitrovszky A., Nagy A., Oszetzky D., Kerekes A., Kugler Sz., Rigó I., Tóth A. and Koós M. (2015). Creation of blue light emitting color centers in nanosized diamond for different applications. In Nanoscience Advances in CBRN Agents Detection, Information and Energy Security (pp. 93-101). Springer Netherlands.
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Other publications:

7. Mitsa V., Holomb R., Marton A., Veres M., Tóth S., **Himics L.**, Lorinczi A. and Popescu M. (2016). Investigation of atmospheric corrosion by photon energy dependent luminescence and Raman spectroscopy in aged and freshly fractured g-, c-As2S3 with photosensitive realgar inclusions. Journal of Non-Crystalline Solids, 453, 23-27.
8. Ignatovych M., Borysenko M., Davydenko L., Borysenko L., Veres M., **Himics L.** and Koós M. (2016). Cerium and europium

nanospecies in quartz glass: synthesis and spectral study. Materialwissenschaft und Werkstofftechnik, 47(2-3), 193-197.

9. Rigó I., Veres M., **Himics L.**, Tóth S., Czitrovszky A., Nagy A. and Fürjes, P. (2016). Comparative analysis of SERS substrates of different morphology. PROCEDIA ENGINEERING.
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