GENERATION OF HIGHLY LUMINESCENT COLOR CENTERS IN NANOCRYSTALLINE DIAMOND (PD106130)

Introduction

In the last decades production of highly luminescent color centers in nanometer sized diamond is one of the most interesting research fields due to the unique properties of nanocrystalline diamond, like biocompatibility, chemical stability and inertness. Some high quality applications, such as quantum technology or biological imaging is in the focus nowadays, however development of reliable single-photon source working at room temperature is still the main challenge for research groups. The emission of color centers covers the spectral range from deep ultraviolet to far infrared. Majority of them are related to impurities like hydrogen, nitrogen and some metals. Color centers could be unambiguously characterized by its emission band, which consists of zero phonon line (ZPL) and vibronic sideband together, even if the ZPL of different impurities are very close to each other. Generally, the ZPL is the spectrally narrowest transition of the color center, while vibronic sideband contains information about the phonon normal modes of a crystal lattice and the strength and symmetry properties of the electron-phonon coupling. Among the impurity-related color centers metal-related impurity centers are particularly interesting due to their relatively low electron-phonon coupling resulting in a narrow (generally 5 meV) and highly intensive ZPL and a weak vibronic sideband.

The aim of my research was to generate and characterize stable, highly luminescent impurity-related color centers in nanodiamond grains and thin films. According to the workplan my research was focused on the following tasks:

1. Applied technologies and treatment processes

1.1. Microwave plasma assisted chemical vapor deposition (MW CVD) system

Construction of the microwave plasma assisted chemical vapor deposition (MW CVD) system was adopted to grow nanocrystalline diamond films under different conditions with simultaneous incorporation of various foreign atoms serving as color centers. This system makes it possible to change the substrate temperature, the working pressure and the methane/hydrogen/argon gas ratio to get nanocrystalline diamond samples with different surface morphology, grain size and amorphous content in the grain boundary region.

Diamond nucleation using bias voltage results in homogenous surface coating of diamond grains. Preparation of sample series was performed under different deposition conditions (substrate temperature, gas ratio). It was found that deposition parameters have remarkable effect on both the properties of the grown nanodiamond films and the incorporation of different impurity atoms, as well as on the formation of defect centers. Morphology of the samples was investigated and it was found that diamond crystallites can be recognized in all of the samples with significant differences in the morphology depending on the deposition parameters. The average grain size of CVD films was determined and we obtained that the average grain size decreases as the methane concentration in the source gas increases. At the same time the substrate temperature has significant influence on the average grain sizes, the higher the substrate temperature, the larger the average grain sizes can be observed.

1.2. Plasma Immersion Ion Implantation (PIII) and Focused Ion Beam (FIB) methods

Low energy Plasma Immersion Ion Implantation (PIII) and Focused Ion Beam (FIB) with different energies, fluences, and types of ions were used to create subsequently complex defect centers in nanodiamond grains. The basic differences between the PIII and the FIB process are the ion sources and the applied ion optics column in FIB system, which focuses ions into a beam. The beam diameter can be reduced to 5–7 nm. During the implantation methods, nanodiamond sample was implanted with He^+ ions first, to create vacancies, followed by the introduction of nitrogen in the form of N_2^+ implantation. Generation of vacancies in diamond with higher grain sizes by helium ion implantation is a well-known method. This small ion is suitable for vacancy creation without considerably damaging the structure in natural diamond, but the subsequent creation of a “good quality” color centers especially in nanodiamond particles with few ten nanometers diameter size has not been solved yet.

The relative number of created vacancies and implantation depth were calculated using Monte Carlo simulations with The Stopping and Range of Ions in Matter (SRIM-2012) code. Simulations showed that both high and low ion energies are suitable for creation of nitrogen-related defect centers in nanodiamond grains using ion implantation.

1.3. Treatment processes

After the implantation of nanodiamond grains high temperature (~750°C) annealing in vacuum was applied for 2 h in order to initiate the vacancy diffusion and to increase the probability of the formation of complex centers. The diamond structure was also partially distorted during the implantation and a part of sp^3 carbon atoms was transformed into sp^2 hybridized state. To decrease the sp^2 carbon content, nanodiamond samples were subjected to another annealing at 450 °C for 5 h in air.

1.4. Qualification methods

Raman scattering with different excitation wavelengths (488 and 785 nm) is a well-known, non-destructive method to verify the quality, the bonding properties and the microstructure, as well as the effect of the incorporated atoms on the structure of the forming nanodiamond grains and films prepared by different methods and deposition conditions. More detailed analysis of the position of diamond Raman peak (~1331 cm^{-1}) could give information about the residual stress rising in the nanodiamond grains through the deposition process, even it may be compressive or tensile type. Moreover study of the Raman spectra of nanodiamond grains in low frequency region (below ~550 cm^{-1}) the Raman active modes among the quasilocal vibrations can be detected.

Photoluminescence measurements were made to detect, analyze and prove the presence of color centers generated by different methods, since color centers in nanocrystalline diamonds exhibit intense luminescence at room temperature from the UV to the infrared spectral region. Photoluminescence measurements at low temperatures (10 K) are also necessary to explore the phonon structure in NCD. The excitation spectroscopy is suited to characterize the absorption features of the generated structural units.

2. Characterization of stable, highly luminescent impurity-related color centers

2.1. Analysis of the spectral parameters in case of the already known silicon-vacancy (SiV) color center

The SiV center has a stable, intense and narrow ZPL around 738 nm, which is right in the middle of the wavelength window of highest optical transparency of tissues, therefore diamond nanoparticles with SiV defects could be promising candidates for applications like in vivo biosensing. Silicon defects in diamond can be produced by ion implantation and also by the incorporation during the growth process. The latter could be realized by introduction of Si atoms into the methane/hydrogen plasma, usually by sputtering of a Si wafer with the plasma itself. Previous reports in the literature presented that the ZPL of the SiV center might be split and broadened, as well as its position spreads in the wavelength range of 733 − 745nm. The aim of our research was to explore the reason of this behavior. It seems to be obvious that the deposition parameters will have remarkable effect on both the properties of the grown nanodiamond films and the incorporation of Si atoms, as well as on the formation of defect centers.

The effect of precursor gas composition and substrate temperature on the spectral characteristics of SiV ZPL, as well as on the emission intensity in nanocrystalline diamond films were investigated. Series of nanodiamond layers were prepared with different methane concentrations and substrate temperatures. Spectral parameters of SiV color center, like peak position, full width at half maximum and integral intensity were correlated with the deposition conditions and the structural features. It was found that diamond crystallites can be recognized in all of the samples with significant differences in the morphology depending on the deposition parameters. The average grain size decreases as the methane concentration in the source gas increases. At the same time the substrate temperature has significant influence on the average grain sizes, the higher the substrate temperature, the larger the average grain sizes can be observed. Based on the Raman spectra the influence of substrate temperature and CH_4 concentration of source gas have impact on the bonding properties and microstructure of the forming films too.

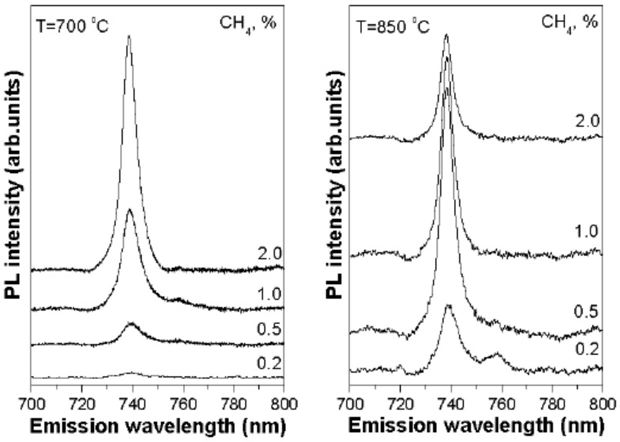

Fig. 1: SiV peak region in the photoluminescence spectra of NCD films prepared at 700°C and 850°C substrate temperatures from gas mixtures of different methane content. The excitation wavelength is 488 nm.

The variation of bonding properties and morphology with deposition conditions presages their influence to the SiV emission features. Fig. 1 shows the 488 nm excited PL spectra in the region of the SiV-related peak for two sample sets, corresponding to 700°C and

850°C substrate temperatures. It was found that the methane content, as well as the grain size has a leading role in the formation of the SiV color center. The methane content affects the SiV PL emission intensity, while substrate temperature has influence to the peak position and linewidths. While the use of 850°C will favor the more ideal emission features of SiV, smaller temperature will lead to SiV emission of higher intensity.

In case of micro- and nanocrystalline samples the linewidth of SiV ensembles is influenced by inhomogeneous broadening, which is especially visible in low temperature spectra, where the homogenous broadening due to phonons that dominates at room temperature is strongly reduced. Several research groups analysed the inhomogeneous broadening of the SiV ZPL. According to their work possible sources of inhomogeneous broadening could be the mechanical stress or the spectral diffusion in diamond, but substantive results were not published yet. The aim of our research was to explore the reason of the inhomogeneous broadening in CVD diamond samples.

We started our research with a completely different supposition, namely the presence of another defect center close to the SiV. It is well known in the literature, that a low concentration of neutral vacancy-related GR1 (abbreviation of General Radiation) center (below $5*10^{12}$ cm^{-3}) is always present in the top layer of the growth surface (a few micrometers deep) of CVD diamond films. Vacancies are created in the surface layer and subsequently migrate to trapping centers or grain boundaries, because they become mobile at about 700 °C, a temperature close to the deposition temperature in the diamond CVD process. In photoluminescence spectra it is quite difficult to separate SiV and GR1 centers from each other at room temperature. Measurements at low temperature show that the GR1 center has a doublet structure with ZPL at 741 and 744 nm. The phonon side band of GR1 center is completely overlapped with the phonon side band of the SiV center. In order to explore the degree of its contribution to the SiV emission spectral shape, whether it appears like unremarkable sideband or is a part of the broad ZPL, it is rewarding to investigate behavior of these color centers under different conditions.

One way is to perform luminescence measurements at low temperature to separate ZPLs of two different defect centers. However these measurements could not be productive if the concentration of the GR1center is too low and its contribution to the intense SiV ZPL is not significant. Another way to get more insight into the emission process, which influences the SiV center’s ZPL parameters, is to increase excitation intensity. Increasing the excitation intensity enhances the generation rate of electron-hole pairs; hence the emission intensity increases also. Therefore an increasing contribution of optical transitions, e.g. the light emission of GR1 center, which causes the additional broadening and change of peak position of SiV ZPL, could also be expected.

The 488 nm (2.54 eV) line of an Ar-ion laser was used for optical excitation; excitation intensity was changed by increasing the laser current. In Fig. 2. the influence of the laser intensity on the emission spectral shape is shown. With increasing excitation intensity the emission band became more intense with asymmetrical broadening caused by significant enhancement in the long wavelength region developed. The maximum of the ZPL shifts towards longer wavelengths and phonon side bands became more dominant and overlapped.

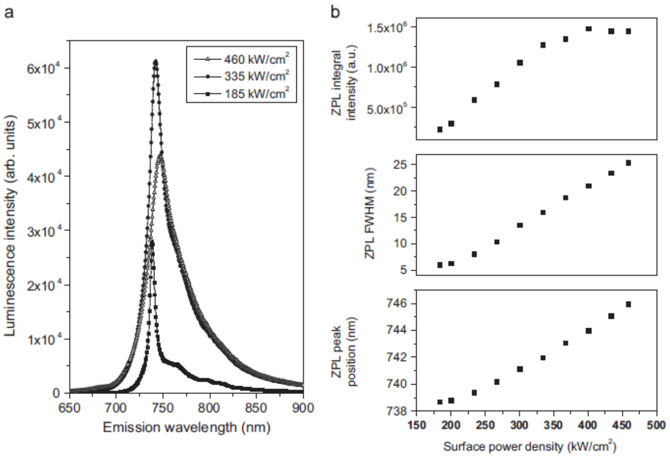

Fig. 2. (a) PL spectra of SiV center measured on diamond sample with increasing excitation intensity at room temperature; (b) variation of the peak position, FWHM and integral intensity of the ZPL with excitation intensity.

Additional photoluminescence measurements were made to confirm the presence of vacancies with different charged states in the environment of the SiV center. It is well known in the literature that beside the neutral vacancy (GR1) there are two more vacancy-related defect, the negatively (V^-) and the positively (V^+) charged vacancy. Concentration of these centers is depending on the diamond structure and the generation type of the vacancy. There are two processes between neutral and charged vacancies. Ionization occurs under UV illumination, where two neutral vacancies (2 GR1) transform into one positively (V^+) and one negatively charged (V^-) vacancy. Another process is the deionization, where one positively (V^+) and one negatively charged (V^-) vacancy transform into two neutral vacancies (2 GR1). This process occurs under heating and also under light illumination in the spectral region from

1.1 to 2.83 eV (1127 - 438 nm) with deionization bands at 2.5 eV (496 nm) and 2.8 eV (443 nm). The laser line of Ar-ion laser used for excitation is 488 nm (2.54 eV), which is very close to the former deionization band of charged vacancies therefore the illumination of the samples by these photons results in the formation of GR1 centers. In the case of lowest excitation intensity contribution of the emission of GR1 center to the measured luminescence band is small compared to the intensive SiV emission. However increased excitation intensity in this deionization photon energy region could generate more neutral vacancy (GR1) compared to the low excitation if positively (V^+) or negatively (V^-) charged vacancies reside in the diamond grain. We have performed experiments by using high intensity excitation of the samples by 2.54 eV photons and at the same time illuminating with 3.05 eV photons which initiate the ionization process of GR1 centers. We observed very impressive change in the spectrum caused by near UV illumination; the narrowing of the ZPL due to diminish of the long wavelength emission as well as the decrease of emission intensity are in good accordance with the ionization of GR1 centers caused by simultaneous light illumination with 3.05 eV photon energy. Consequently we confirmed the presence of vacancies with different charged states and we stated that the formation of GR1 center could explain the large broadening and red-shift of the emission caused by the intensive excitation of diamond grains.

2.2. Creation of new, highly luminescent color centers in nanodiamond grains

2.2.1. Deep blue light emitting nitrogen-related color center (N3)

Creation of near UV light emitting defect center, the N3 center, was prepared successfully in nanodiamond crystals of average sizes smaller than 20 nm. The center consists of three nitrogen atoms surrounding a carbon vacancy and it has unpaired electron spin, which means that it is also suitable for qubit formation. The emission in deep blue wavelength region offers application potential as solid state lasers and light emitting diodes too. Plasma Immersion Ion Implantation (PIII) and Focused Ion Beam (FIB) of nanodiamond powder with different energies, fluences, and types of ions were used to create complex defect centers. After the implantation high temperature (~750°C) annealing in vacuum was applied for 2 h to the samples in order to initiate the vacancy diffusion and to increase the probability of the formation of complex centers. The diamond structure was distorted partially during the implantation and a part of sp^3 carbon atoms was transformed into sp^2 hybridized state. To decrease the sp^2 carbon, the content samples were subjected to another annealing at 450 °C for 5 h in air. The effect of different implantation techniques and heat treatments on the nanodiamond samples was monitored by micro-Raman spectroscopy. Implantation of ND sample results in an increasing dominance of sp^2 carbon content. The heat treatments result in the decrease of sp^2 hybridized carbon content in implanted samples and the diamond peak became well detectable again.

To verify the formation of nitrogen-related centers in the ND grains, the samples were analyzed by photoluminescence spectroscopy. Detailed analysis of the ZPL peak position and phonon side band performed at low and room temperatures proves the characteristics of the N3 center. As a result of PIII/FIB implantation and complex heat treatments the room temperature PL spectrum changed dramatically (Fig. 3.). It is dominated by a relatively narrow emission band, with maxima at 2.98 eV (416 nm) and 2.83 eV (438 nm) and a weaker shoulder appears at 2.7 eV (459 nm) photon energy in all cases. Based on the fitted peak positions the first one corresponds to the ZPL of N3 optical center, while the second and the third peaks are its phonon replica.

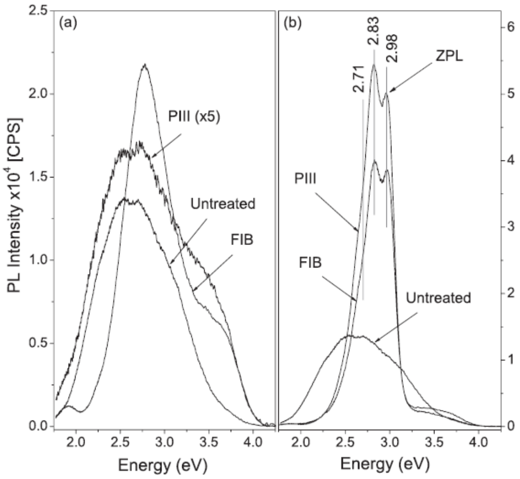

Fig.3. Room temperature PL spectra excited by E_{ex}=4.597 eV photon energy of untreated and implanted (using PIII and FIB techniques) diamond nanocrystals (a) before and (b) after heat treatments.

We have demonstrated that the plasma immersion ion implantation and focused ion beam technique combined with complex heat treatments is suitable for creation of a relatively intensive and narrow emission band near the deep blue wavelength region in nanodiamond particles having average crystallite size of around 12 nm. The observed emission band is related to nitrogen-vacancy complexes and it can be identified as the emission of the N3 optical center.

2.2.2. Creation of near-infrared emitting optical center related to nickel-silicon impurity complex in nanodiamond grains

Creation of near-infrared emitting defect center, the Ni-Si complex center, was prepared successfully by CVD method in diamond crystals of average sizes smaller than 120 nm. Defect centers related to different metal impurities are particularly interesting because of the narrow (generally 5 meV) ZPL in the near-infrared region with a weak vibronic sideband caused by the relatively low electron-phonon coupling. The aim of our research was to form metal-related defect centers with intensive, narrow-band emission in the near-infrared region through the CVD growth process of nanodiamond. Especially in that wavelength region (830-880 nm) where a few emission peaks were documented, moreover the identification and assignation of the observed emission lines to a definite defect structure was not performed.

Numerous nanodiamond grains prepared at different deposition conditions were scanned under the focused laser beam and the fluorescence was measured in the 800-900 nm (1.549-1.377 eV) range. The observed intensive emissions in the 860-871 nm (1.441-1.423 eV) region are related to the ZPL of a complex optical center formed under the growth process of nanodiamond grains prepared at the same (Fig.4a.) and different (Fig.4b.) deposition conditions. These spectra were selected to represent characteristic spectral shape of light emission monitored in the interesting wavelength region. Advantageous features of this optical center are the narrow linewidth of the ZPL and also the concentration of emitted light into ZPL even at room temperature.

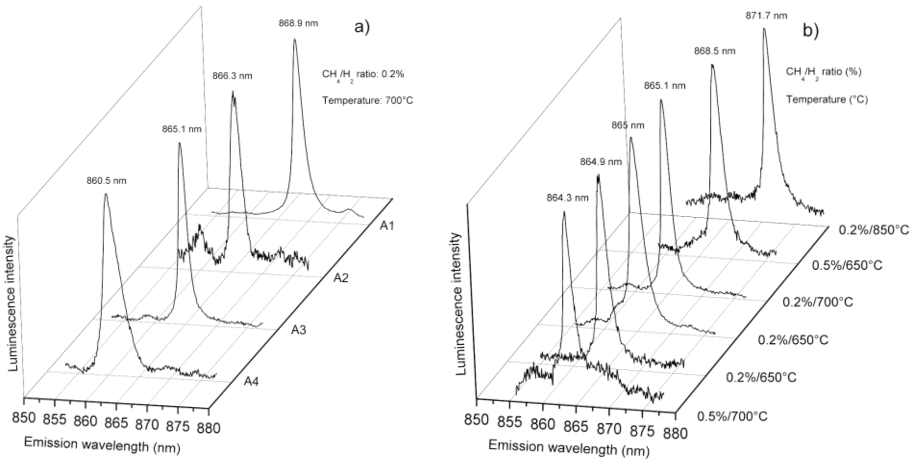

Fig.4. ZPL spectral shape of Ni-Si related complex impurity center recorded by 488 nm (2.54 eV) laser excitation at room temperature on nanograins deposited (a) under the same conditions and (b) under different conditions.

Majority of nanodiamond grains examined in this work emits near 865 nm (1.433 eV), thus we use it as characteristic ZPL's wavelength of the complex optical center. The observed narrow bandwidth of the 865 nm ZPL and the weak electron-phonon coupling as the light emission is concentrated into the ZPL, indicate the metal impurity content of the optical center. According to the literature data Ni-based color centers have intensive emission in this wavelength region, but those are differing from the 865 nm fluorescence system. Regarding the incorporation of silicon impurity from the substrate material into diamond grains through the growth process, silicon impurity atom as defect center component could also be taken into account. A more insight into the structure and impurity content of the complex color center we obtain by the detailed analysis of the vibronic sideband of the 865 nm ZPL.

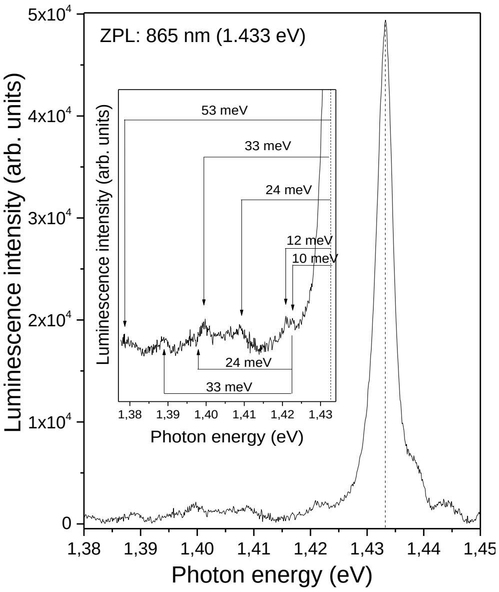

Fig.5. Spectral feature of the 865 nm fluorescence system excited by 488 nm (2.54 eV) at room temperature in nanodiamond grain. The inset shows the vibronic sideband structure of the 865 nm ZPL on a stretched intensity scale. The observed sideband features are marked and those energies are signed in meV with respect to the ZPL peak position.

If a defect center contains heavy impurity atom the frequency and resonance width of the quasilocal vibration could be estimated. The frequency and resonance width of quasilocal vibrations for some defect structure containing Ni and Si impurity atoms (1Ni+1Si, 1Ni+2Si, 2Ni+1Si and 2Ni+2Si) were calculated. The calculated values and the measured PL features indicate the presence of Ni and Si atoms in the complex optical center which accounts for the

865 nm (1.433 eV) fluorescence system. The atomic bonding structure of the complex optical center can be monitored by a powerful non-destructive method, the Raman-scattering measurements. Study of the Raman spectra of nanodiamond grains in low frequency range (below ~550 cm^{-1}) the Raman active modes among the quasilocal vibrations can be detected.

Fig. 6. shows the Raman scattering spectrum measured by 785 nm diode laser excitation of the nanodiamond sample. In our setup the focusing of the excitation light and the collection of the fluorescence and Raman scattering is performed by using the same microscope objective. Therefore the fluorescence and Raman spectra are recorded from the same sample volume. Raman scattering of low frequency local modes assigned to Ni-Si bonding structure clearly seen. Raman scattering study performed in low frequency region confirmed that the optical center contains Ni and Si atoms together.

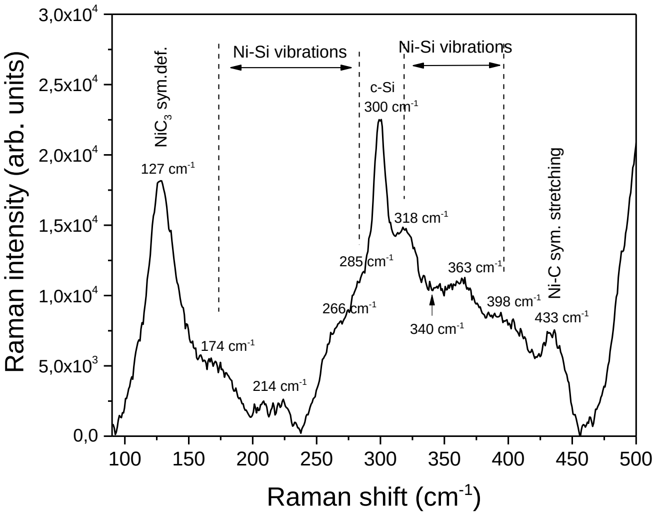

Fig.6. Raman scattering spectrum in the low frequency region measured by 785 nm diode laser excitation of nanodiamond sample. The assignments of the peaks are depicted.

According to the detailed analysis of the spectral features of the ZPL and quasilocal modes of the vibronic sideband a complex center containing Ni and Si atoms could be accounted for this emission. The inclusion of Ni and Si impurity atoms in the complex optical center was strengthened by micro-Raman spectroscopy performed in the frequency range due to quasilocal vibrations of the vibronic sideband.

Some additional measurements should be performed to map structural arrangement of this complex impurity center, since Ni ions could occupy substitutional, interstitial and divacancy positions equally. Inclusion of a vacancy into the complex impurity center may help to explain variation of the ZPL peak positions and linewidths even in nanodiamond grains prepared at the same conditions. Soft defect centers are expected to be more sensitive to the change of local stress field compared to the impurity centers related to transition metals. Preliminary results on the residual stress determined from the position of diamond Raman peak measured on different nanodiamond grains exhibits different values in the range of (-1.21)-1.19 GPa. These results indicate the variation of local field even it may be compressive or tensile type in nanodiamond grains prepared under same conditions.