



Effective implantation of light emitting centers by plasma immersion ion implantation and focused ion beam methods into nanosized diamond



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ABSTRACT

Two different implantation techniques, plasma immersion ion implantation and focused ion beam, were used to introduce nitrogen ions into detonation nanodiamond crystals with the aim to create nitrogen-vacancy related optically active centers of light emission in near UV region. Previously samples were subjected to a defect creation process by helium irradiation in both cases. Heat treatments at different temperatures (750 °C, 450 °C) were applied in order to initiate the formation of nitrogen-vacancy related complex centers and to decrease the sp² carbon content formed under different treatments. As a result, a relatively narrow and intensive emission band with fine structure at 2.98, 2.83 and 2.71 eV photon energies was observed in the light emission spectrum. It was assigned to the N3 complex defect center. The formation of this defect center can be expected by taking into account the relatively high dose of implanted nitrogen ions and the overlapped depth distribution of vacancies and nitrogen. The calculated depth profiles distribution for both implanted nitrogen and helium by SRIM simulation support this expectation.

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1. Introduction

The nanodiamond is one of the most promising materials for many new type applications in different fields as a bio-marking, quantum computing or sub-diffraction imaging. The majority of these applications based on the light emission properties of defect centers containing nanodiamond crystals [1,2]. The major part of light emitting centers in diamond is related to the nitrogen impurity. There are simple (NV) and more complex (N3) forms of nitrogen related color centers that were investigated in diamond. Some of them were created artificially, but majority were studied in natural crystals. The subsequent creation of a “good quality” color centers especially in nanodiamond particles with few ten nanometers diameter size has not been solved yet. In many cases the introduction of required impurity atoms into nanodiamond matrix is a very complex and expensive process, which needs modern appliances and high level of knowledge. A simple method as the ball milling of color centers containing large diamond crystals is

less effective. The removing of sp² carbon content, generated under milling process, needs further complicated treatments. The identification and separation of nanodiamond (ND) particles with required color centers are also difficult from milled powder. Another possible method is the adaptation of high energy ion implantation technique which was successfully used in large diamond crystals and CVD films [3,4]. The disadvantages are the high damage of diamond structure and the expensive and complicated realization due to the applied high ion energies and not widely available ion accelerators.

Our aim was to create nitrogen related complex color centers by using simple and widely available techniques. In this aspect the low energy ion implantation is an effective and well-known method used for subsequent introduction of impurities and modification of structural properties of materials [5]. Numerous advantages, like controllable impurity density and the relatively shallow depth distribution of ions, make this technique favorable for implantation process of nanodiamond crystals. On the other hand, the properly chosen ion energy is feasible to minimize the damage of ND particles, but still allows the ions to penetrate into the structure.

In our experiments the low energy ion implantation was performed by using plasma immersion ion implantation (PIII) [6] and

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Table 1
The applied ion energies and fluxes in PIII and FIB experiments.

Type of technique	PIII		FIB
Type of ions	He ⁺ /N ₂ ⁺		He ⁺ /N ₂ ⁺
Ion energy (keV)	30	20	2
Ion flux (1 cm ⁻²)	1 × 10 ¹⁷	1 × 10 ¹⁷	1 × 10 ¹⁵

focused ion beam (FIB) [7] techniques, which are available in many laboratories. These methods can be used for surface modification as well as for shallow ion implantation and modification of the sample properties [8]. In contrast with generally used high ion energy implantation, reported in many papers, in which the ion energy often exceeds several hundreds keV or MeV, the applied few tens keV ion energy in PIII case and the further reduction to a few keV in FIB technique are expected to have a less destructive impact on the structure. 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. While both of the techniques are suitable to introduce impurity atoms into the structure, the efficiency of the implantation and the effect on the structure may be different, which could especially be important when the targets are nano-sized diamond particles and the aim of the ion implantation is the creation of color centers. Differences can be caused not only by different ion energies, but also by the fundamental differences of the two implantation techniques. While under the plasma immersion ion implantation, which is a well-known tool for surface treatment, the whole surface of nanodiamond particles exposed to the impact of the relatively high concentration of ions, the focused ion beam is a tool to introduce desired ions directly into the ND crystal volume without substantially surface treatment.

In this work we report about the dramatical changes of the emission spectrum in the deep blue region and successful introduction of nitrogen impurities into detonated ND particles by using plasma immersion ion implantation and focused ion beam techniques combined with subsequent heat treatments at different temperatures and atmospheres. The created emission is related to the N3 optically active complex defect center, which was supported by photoluminescence (PL) measurements and Fourier Transform Infrared (FTIR) spectroscopy.

2. Experimental

The nanodiamond slurry, prepared by 3 h long ultrasonication of commercially available detonation ND powder (Neomond Ltd.) and distilled water mixture, was dripped into a stainless ring placed on a silicon wafer. The concentration of nanodiamond in the suspension was 1.5 mg/ml. The samples were dried in air for 48–72 h at room temperature. After the removal of the ring a circular shape of ND “film” was left on the silicon surface.

In our experiments we have used nitrogen ions (N₂⁺), as a most important impurity in diamond responsible to many interesting color centers, to create a deep blue light emitting complexes. Previously, samples were subjected to a He⁺ ion treatment in both cases, with the aim to generate vacancies in crystals, necessary to the formation of nitrogen-vacancy complexes. The implantation parameters are shown in Table 1.

Implantation process was performed by using PIII and FIB techniques. In plasma immersion ion implantation experiments an inductively coupled RF plasma was maintained by 50 W of power at 27.13 MHz. Implantation was realized by applying 30 kV accelerating voltage with pulse-duration of 5 μs length. For study of the effect of ion implantation energy on the ND structure the accelerating voltage was decreased to 20 kV without changing the other implantation parameters. In FIB case samples were scanned by ion

beam and the used accelerating voltage was decreased to 2 kV with the aim to minimize the destruction of the structure as possible. The currents were 4 μA at N₂⁺ and 4.7 μA at He⁺ ions.

To release the stress in the implanted ND crystals and to restore the diamond structure as well as to remove the non-diamond content from the samples were heat treated at 750 °C for 2 h in vacuum and at 450 °C for 5 h in air.

Changes in bonding structure were detected with Raman spectroscopy and Fourier transform infrared spectroscopy. The Raman spectra of the samples were recorded on a Renishaw 1000 spectrometer equipped with a Leica microscope. The excitation was performed using the 488 nm line of an argon ion laser. After baseline correction all the spectra were normalized to their maximum intensity in the 1000–2000 cm⁻¹ region and shifted along the ordinate for better visibility. FTIR spectra were recorded on a Bruker Tensor 37 spectrometer attached to a microscope in the 600–2000 cm⁻¹ region with 2 cm⁻¹ resolution.

Photoluminescence (PL) spectra were investigated at room and at low temperatures in front face geometry by using a Horiba Jobin Yvon FL3-22 fluorometer with 450 W xenon lamp excitation source. The PL spectra presented in this paper were excited by 4.59 eV photon energy. Spectral distribution of luminescence was analyzed in the 1.75–4 eV emission photon energy region with spectral resolution of 4–17 meV. The measured spectra were corrected for the spectral response of the system and for the excitation intensity as well.

3. Results and discussion

SRIM calculations [9] were performed to determine the depth distribution of implanted ions as well as that of the generated vacancies. The results of SRIM calculations provide also some evidence on the formation of nitrogen-vacancy related complexes. The input parameters for each calculation were 3.15 g/cm³ for density of nanodiamond, 45 eV for displacement energy and 4.3 eV for surface binding energy [10–12].

Fig. 1 shows the depth distribution of vacancies created by He⁺ irradiation and implanted nitrogen atoms calculated using the SRIM code for PIII and FIB implantation parameters. The nitrogen distribution shows a shallower character in the FIB case compared to the PIII cases (Fig. 1a). Majority of nitrogen ions calculated with 2 keV ion energy stops in depth of around 5 nm, while the increase of the ion energies to 20 and 30 keV result in shift of the maxima to 35 and 50 nm, respectively. The vacancy distributions generated by helium implantation show a similar behavior (Fig. 1b). Helium ions with lower ion energy create vacancies in the 1–28 nm range, while for higher energies the depth distributions are broadened and the maxima shifted to the deeper regions. The formation of nitrogen-vacancy related complexes is most probable in the depth where the nitrogen and vacancy concentrations are maximal. According to SRIM, in our cases it was realized maximally for the FIB (2 keV) implantation, but the formation of nitrogen-vacancy complexes can be expected under PIII processes too, if the number of vacancies generated in result of nitrogen implantation are also taken into account (Fig. 1c). Vacancies can also be generated by nitrogen ions, which modify the final vacancy-nitrogen ratio in implanted samples, but the depth distribution shows a slightly shallower character as these ions have not enough energy to kick out carbon atoms at the final stage of their trajectory. Taking this into account and based on the calculated results it can be stated that the formation of nitrogen-vacancy complexes is most probably in few nanometers (1–8 nm) depth in the FIB case, in 5–50 nm depth for PIII with 20 keV and in 5–75 nm range for PIII with 30 keV ion energies. The formation of above-mentioned defects was supported experimentally by the appearance of a new emission band in PL spectra.

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