Journal of Luminescence 179 (2016) 59–63

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Full Length Article

Creation and characterization of He-related color centers in diamond

J. Forneris [a,b,c,*], A. Tengattini [b,a,c], S. Ditalia Tchernij [b,a,c], F. Picollo [a,b,c], A. Battiato [b,a,c], P. Traina [d], I.P. Degiovanni [d], E. Moreva [d], G. Brida [d], V. Grilj [e], N. Skukan [e], M. Jakšić [e], M. Genovese [a,c,d], P. Olivero [b,a,c]

[a] Istituto Nazionale di Fisica Nucleare (INFN), Sez. Torino, via P. Giuria 1, 10125 Torino, Italy
[b] Physics Department and "NIS" Inter-departmental Centre - University of Torino, 10125 Torino, Italy
[c] Consorzio Nazionale Interuniversitario per le Scienze Fisiche della Materia (CNISM), Sez. Torino, Torino, Italy
[d] Istituto Nazionale di Ricerca Metrologica (INRiM), Strada delle Cacce 91, 10135 Torino, Italy
[e] Ruđer Bošković Institute, Bijenicka 54, P.O. Box 180, 10002 Zagreb, Croatia

ARTICLE INFO

Article history:
Received 13 May 2016
Received in revised form
15 June 2016
Accepted 17 June 2016
Available online 25 June 2016

Keywords:
Diamond
Color center
Defect
Ion implantation
Photoluminescence

ABSTRACT

Diamond is a promising material for the development of emerging applications in quantum optics, quantum information and quantum sensing. The fabrication and characterization of novel luminescent defects with suitable opto-physical properties is therefore of primary importance for further advances in these research fields.

In this work we report on the investigation in the formation of photoluminescent (PL) defects upon MeV He implantation in diamond. Such color centers, previously reported only in electroluminescence and cathodoluminescence regime, exhibited two sharp emission lines at 536.5 nm and 560.5 nm, without significant phonon sidebands.

A strong correlation between the PL intensities of the above-mentioned emission lines and the He implantation fluence was found in the 10^{15}–10^{17} cm^{-2} fluence range. The PL emission features were not detected in control samples, i.e. samples that were either unirradiated or irradiated with different ion species (H, C). Therefore, the PL features are attributed to optically active defects in the diamond matrix associated with He impurities. The intensity of the 536.5 nm and 560.5 nm emission lines was investigated as a function of the annealing temperature of the diamond substrate. The emission was observed upon annealing at temperatures higher than 500 °C, at the expenses of the concurrently decreasing neutral-vacancy-related GR1 emission intensity. Therefore, our findings indicate that the luminescence originates from the formation of a stable lattice defect. Finally, photoluminescence from He-related defects was observed under different laser excitations wavelengths (i.e. 532 nm and 405 nm), thus providing promising evidence of a broad spectral range for optical stimulation.

1. Introduction

In the last decade diamond has been thoroughly investigated as a promising material for applications in the field of quantum optics, due to the discovery and the characterization of several luminescent point defects with appealing light emission and spin properties [1–3].

Up to date, the most prominent system in this field is the negatively-charged nitrogen-vacancy center (NV^-), whose well established high quantum efficiency, stability at room temperature and appealing spin properties structure represent an intriguing potential for applications in quantum photonics, cryptography, sensing and computing [4–9]. On the other hand, some of its limitations (relatively long radiative lifetime, charge state blinking and broad spectral emission [10]) led to the exploration of alternative luminescent centers for single-photon source applications, such as the Si-V center [11,12], Ni- [13–15], Eu- [16] and Ge-related [17,18] impurities, as well as radiation-damage related defects [19] and other bright NIR emitters [20,21], which demonstrated up to tenfold higher emission rates, as well as a strongly polarized and spectrally narrower emission. Thus, the fabrication of novel luminescent defects with desirable properties upon the implantation of selected ion species still represents a crucial strategy to achieve further advances in the aforementioned research fields.

In this work, we report on the investigation of the photoluminescence (PL) properties of optically active defects in diamond obtained upon the implantation of MeV He^+ ions and subsequent thermal annealing at temperatures >500 °C. The measured PL

* Corresponding author at: Istituto Nazionale di Fisica Nucleare (INFN), Sez. Torino, via P. Giuria 1, 10125 Torino, Italy. Tel.: +39 011 670 7306.
E-mail address: forneris@to.infn.it (J. Forneris).

http://dx.doi.org/10.1016/j.jlumin.2016.06.039
0022-2313/

emission consists of two sharp and intense emission lines at 536.5 nm and 560.5 nm, characterized by a negligible phonon coupling. These emission lines were reported, together with a series of other minor PL peaks, in two previous cathodoluminescence studies on He-implanted IIa-type diamond [22,23], and more recently were identified in electroluminescence spectra acquired from He-implanted diamond devices [24]. Up to date, the excitation of these emission lines was never reported in PL regime, despite the wider availability of this characterization technique. This somewhat surprising evidence is motivated by the spectral range of this emission, which is typically filtered out in the most commonly adopted PL confocal microscopes, as it is comprised between the excitation wavelength (typically 532 nm) and the first-order Raman line (at 572.5 nm for the above-mentioned excitation). Differently from the commonly adopted experimental PL setups, in the present work two alternative laser excitation wavelengths (i.e., 532 nm in combination with narrowband notch filtering, and 405 nm) were adopted.

2. Experimental

The experiments were performed on a set of type-IIa single-crystal diamond samples: 3 nominally identical "optical grade" $3 \times 3 \times 0.3\ mm^3$ substrates by ElementSix (samples #1–3), with respectively < 1 ppm and < 0.05 ppm concentrations of substitutional nitrogen and boron, and a $2 \times 2 \times 0.3\ mm^3$ "detector grade" ElementSix substrate (sample #4) with < 5 ppb nitrogen and boron concentrations. He implantations were performed at the AN2000 microbeam line of the INFN National Laboratories of Legnaro. Several $300 \times 300\ \mu m^2$ regions were homogeneously irradiated on sample #1 with a 1.3 MeV He^+ raster scanning micro-beam at fluences of $1 \times 10^{16}\ cm^{-2}$, and $2 \times 10^{16}\ cm^{-2}$. An additional $100 \times 100\ \mu m^2$ irradiation was performed on sample #2 with a 1 MeV He^+ beam at a $1 \times 10^{15}\ cm^{-2}$ fluence. A $200 \times 200\ \mu m^2$ implantation at $5 \times 10^{14}\ cm^{-2}$ fluence was performed on sample #4 with a 1.8 MeV He^+ beam. Sample #3 underwent a control implantation with 6 MeV C+ ions at $2 \times 10^{15}\ cm^{-2}$ fluence, at the Laboratory for Ion Beam Interactions of the Ruđer Bošković Institute (Zagreb). The implantation fluence was chosen to obtain a similar vacancy density in the diamond substrate in correspondence of the Bragg peak (i.e. 1×10^{22} vacancies cm^{-3}) as that achieved in the case of 1.8 MeV He^+ implantation at $1.5 \times 10^{16}\ cm^{-2}$ fluence [25]. After ion implantation, samples #1–3 were annealed in vacuum at 1000 °C for 2 h to promote the formation and optical activation of the luminescent defects. Sample #4 underwent subsequent annealing steps in vacuum (2 h each) at increasing temperatures up to 1000 °C, to investigate the role of thermal processing in the defect formation. After each thermal treatment, the ion-implanted region of sample #4 was characterized in PL emission. PL spectra were acquired with a Horiba Jobin Yvon HR800 Raman micro-spectrometer equipped with a 1800 mm^{-1} diffraction grating. The optical excitation was provided by a continuous 532 nm laser focused with a 20× air objective. The excitation radiation was filtered out from the CCD detection system by a narrow-band notch filter (Super Notch Plus 532 nm filter, 6.0 optical density, < 10 nm spectral bandwidth).

PL measurements at a lower excitation wavelength were performed using a confocal microscope at the Italian National Institute for Metrological Research (INRiM). In this case, the optical excitation was provided by a continuous 405 nm laser focused with a 100× air objective. The PL signal was then acquired by a Si-single-photon-avalanche photo-diode (SPAD) operating in Geiger mode. The use of a dichroic mirror (Semrock 442 nm laser BrightLine) and the optical filters (Thorlabs FEL0500) allowed spectral measurements at wavelengths larger than 500 nm. The PL spectra were acquired using a single-grating monochromator (1600 grooves mm^{-1}, 600 nm blaze) connected to the afore-mentioned SPAD.

3. Results and discussion

3.1. Photoluminescence features of He-implanted diamond

Photoluminescence measurements with 532 nm excitation were acquired in the 533–800 nm spectral range from the regions implanted at increasing ion fluences of samples #1 and #2. In order to provide a quantitative comparison between the different emission intensities, the PL spectra were normalized to the first-order diamond Raman peak measured at 572.5 nm. The resulting spectra are shown in Fig. 1, together with a control PL spectrum acquired from an unimplanted region of sample #1.

The PL spectrum of the unimplanted sample (Fig. 1a) exhibits the typical features of an "optical grade" diamond substrate: the intense first-order Raman peak at 572.5 nm (i.e. 1332 cm^{-1} Raman shift), the zero-phonon lines (ZPLs) of the NV0 and NV^- centers respectively at 575 nm and 638 nm, together with the corresponding phonon replica at higher wavelengths [4]. Apart from the well-established increase in NV emission intensity, the PL spectra from the implanted regions (Fig. 1b–d) revealed two sharp (< 2 nm FWHM) and intense peaks at 536.5 nm and 560.5 nm, together with an emission band in the 580–630 nm spectral range (highlighted in blue in Fig. 1d for ease of view). This latter feature cannot be attributed to Raman transitions (as confirmed with subsequent PL measurements with 405 nm excitation, see below), and it is unlikely to be related to either phonon replica of the NV^0 and NV^- centers, due to the high intensity contrast with respect to the baseline of the NV^0 emission spectrum at wavelengths > 610 nm. More likely, it is to be attributed to the phonon sideband of the 560.5 nm transition, consistently with what reported in Ref. [23]. The intensity of these spectral features displayed a clear correlation with the implantation fluence (Fig. 2). Additionally, a weak peak at 740 nm, observed at the lowest implantation fluence, is attributed to residual radiation-induced vacancies (GR1 centers), i.e. to isolated vacancies which were not completely annealed out upon thermal treatment [22,24].

The PL spectrum is similar to those reported in previous works in both CL [22,23] and EL [24] regimes. In addition, the complex series of emission lines observed in the 536–575 nm range reported in Ref. [23] was not observed, neither in the present experiment nor in previous EL investigations of He implanted diamond [24].

It is worth noting that the 536.5 nm and 560.5 nm luminescence does not correspond to any emission line associated with the atomic He spectrum [26]. The origin of the PL emission should then be either attributed to the formation of stable lattice defects, whose abundance correlates with the He implantation fluence [23], or to the modification of the above-mentioned atomic He emission spectrum by surrounding radiation-induced defects [22].

With the purpose of further strengthening the attribution of the PL emissions at 536.5 nm and 560.5 nm to He-related defects, additional PL measurements were acquired from sample #3, after 6 MeV C^+ implantation and thermal annealing. The emission spectrum (Fig. 1e) clearly exhibits the typical features of NV^0 and NV^- emissions, together with a residual component of GR1 centers at.

740 nm. In this case, the emission lines at 536.5 nm and 560.5 nm could not be detected within the experimental sensitivity. More so, it is worth mentioning that also the emission band in the 580–630 nm region was not observed, thus preventing its attribution as a generic radiation-induced defect, in agreement with the attribution to a phonon sideband of the 560.5 nm peak [23].

Even if the reported spectra do not allow a fully conclusive attribution, which can only be provided with stress-dependent PL