# He-Related Luminescent Defects in Ion-Implanted Diamond

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## INTRODUCTION

Diamond is a promising material for the development of emerging quantum technologies due to the availability of a large number of "color centers", i.e. optically-active lattice defects with appealing opto-physical properties. The fabrication, identification and exploitation of new classes of color centers in diamond is therefore important for further advances in this research field. In the present paper we report about the fabrication of photoluminescent defects in diamond upon MeV $He^+$ implantation in diamond, which was previously observed only in electroluminescence (EL) and cathodo-luminescence (CL) regime [1,2]. An investigation in their spectral emission features and an attribution to He-related defects was performed by investigating the photoluminescence (PL) emission at different implantation fluences and exploiting different excitation laser wavelengths.

## SAMPLE FABRICATION AND PROCESSING

This study was performed on a commercial synthetic single-crystal diamond substrate grown by Chemical Vapor Deposition (CVD) from ElementSix. The $3\times3\times0.5$ mm$^3$ sample is classified as "optical grade" by the supplier, with nominal boron and nitrogen concentrations of <1 ppm and <0.05 ppm, respectively. The sample is cut along the [100] crystal direction and optically polished on the two opposite large faces.

Ion implantations were performed at the microbeam line of the AN2000 accelerator of the INFN National Laboratories of Legnaro (INFN-LNL) by raster scanning across one of the polished surfaces a 1.3 MeV $He^+$ microbeam (~10 µm spot size) over three $300\times300$ µm$^2$ areas at increasing fluences of $1\times10^{16}$ cm$^{-2}$, $2\times10^{16}$ cm$^{-2}$, and $1\times10^{17}$ cm$^{-2}$.
After ion implantation, the sample underwent a thermal annealing in vacuum at 1000 °C for 2 hours, to promote the formation of optically active defects associated with the ion impurities implanted at the end of the penetration range (2.2 µm, according to SRIM simulations [3] performed with the 2013.00 code version). MeV ion irradiation also resulted in the introduction of structural damage in the diamond lattice (~60 vacancies/ion, mainly concentrated at the end of the ion range). Radiation damage is partially recovered upon the afore-mentioned thermal treatment, which promotes the reduction of the vacancy density at temperatures higher than 750 °C [4]. However, the accumulation of damage due to high-fluence implantations eventually results in the amorphization of the diamond crystal when a critical vacancy density threshold of $9\times10^{22}$ cm$^{-3}$ [5] is exceeded. In this case, the amorphized volume was converted to a graphitic phase upon the same thermal treatment performed to ensure the formation of luminescent defects. In particular, the highest implantation fluence adopted in this work ($1\times10^{17}$ cm$^{-2}$) was sufficient to graphitize the irradiated region, thus enabling to identify the role of the graphitic phase in the luminescent emission produced upon ion implantation.

## PHOTOLUMINESCENCES MEASUREMENTS

PL spectra were acquired from the irradiated sample using a Horiba Jobin Yvon HR800 Raman micro-spectrometer equipped with a 1800 mm$^{-1}$ diffraction grating. The optical stimulation was provided by a CW laser with 532 nm excitation wavelength, focused with 20× air objective, on a ~5 µm spot size and with a ~3 µm focal depth. The PL emission was acquired by a CCD detection system. The excitation radiation was filtered by a narrowband notch filter.

Additional PL spectra were acquired at a lower excitation wavelength, using a confocal microscope at the Italian National Institute for Metrological Research (INRiM). In this case a continuous 405 nm laser excitation was focused on the sample by a 100× air objective. The luminescence was then detected using a Silicon single-photon avalanche photodiode (Excelitas SPCM-AQRH-13) operating in Geiger mode. In this case, the spectral analysis of the substrate was performed using a single-grating monochromator (Horiba iHR320, 1600 mm$^{-1}$ diffraction grating, 600 nm blaze) installed between the pinhole of the confocal microscope and the aforementioned SPAD.

## RESULTS

Photoluminescence spectra were acquired from different regions of the sample under 532 nm excitation. The measurements are reported in the 530-625 nm spectral range in Fig. 1. A PL spectrum acquired from an unimplanted region of the same substrate is also shown for reference.

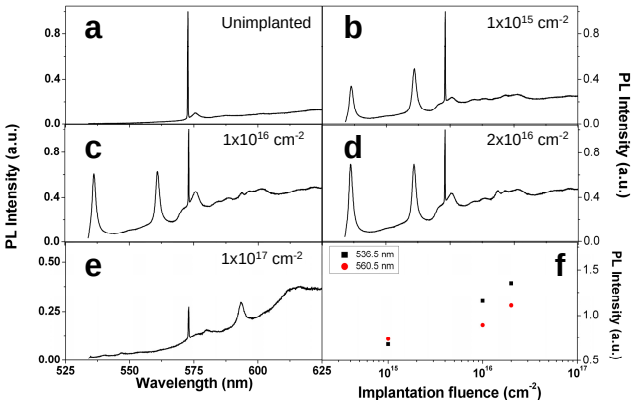


Fig. 1: a) PL spectrum of an unimplanted region of the substrate under investigation. b)-e): PL spectra acquired from sample regions implanted at increasing fluences in the 1×1016-1×1017 cm2 range. The highest ion fluence (1×1017 cm-2) was sufficient to achieve diamond graphitization at the end of the penetration range. f) The ZPL intensity of the He-related emission lines is plotted against the corresponding implantation fluence.

The PL intensity of the spectra corresponding to the unimplanted region (Fig. 1a) and the regions irradiated at $1\times10^{16}$ $cm^{-2}$ and $2\times10^{16}$ $cm^{-2}$ fluences was normalized to the first-order Raman peak of diamond at 572.5 nm (1332 $cm^{-1}$). On the other hand, the area implanted at the highest He fluence exhibited a strong modification in both its structural and luminescence properties, with a significant decrease in the first order Raman peak of diamond. The whole spectrum showed a periodic intensity modulation, which was attributed to interference fringes caused by multiple internal reflections of the broad luminescence emission occurring between the sample surface and the buried damaged layer [6]. This measurement indicates that the implanted region was converted to a graphitic phase upon high-dose irradiation and the subsequent thermal annealing. The PL spectrum at the $1\times10^{17}$ $cm^{-2}$ could not therefore be normalized consistently with the other measurements. The PL spectrum of the unimplanted sample (**Fig. 1a**) exhibits the typical features of diamond substrate with a large concentration of native NV centers: an intense first-order Raman peak at 572.5 nm (i.e. 1332 $cm^{-1}$ Raman shift), the zero-phonon line (ZPL) of the $NV^0$ emission at 575 nm together with the its phonon replica at higher wavelengths [3]. The PL spectra from the implanted regions (Figs. 1b-1d) displayed two additional sharp (<2 nm FWHM) and intense peaks centered at 536.5 nm and 560.5 nm. The intensity of these emission lines exhibited a correlation with the He implantation fluence (**Fig. 1f**). The PL spectrum is similar to those reported in previous works in both EL [1] and CL [2] regimes. Most remarkably, the absence of the PL spectral lines at 536.5 nm and 560.5 nm in the region implanted at $1\times10^{17}$ $cm^{-2}$ He fluence indicates that these emission lines are associated with defects in the diamond lattice and that they cannot be related to the presence of a graphitic/amorphous phase. The reported spectra indicate therefore that the presence of He atoms plays a key role in the formation of a specific optical center in two possible charge states, or alternatively of two types of He-related complexes. This hypothesis is supported by spectral measurement acquired on samples implanted with 6 MeV $C^{3+}$ ions, where the two afore-mentioned He-related emission lines were not observed within the instrumental sensitivity [7]. The PL emission of the region implanted with 1.3 MeV $He^+$ ions at $1\times10^{16}$ $cm^{-2}$ fluence was also investigated under 405 nm excitation. The PL spectrum is compared in Fig. 2 with the corresponding PL spectrum acquired under 532 nm excitation. Both the 536.5 nm and 560.5 nm emission lines are clearly visibile under 405 nm excitation, indicating that this excitation wavelength is effective at optically stimulating the photoluminescence of He-related defects.

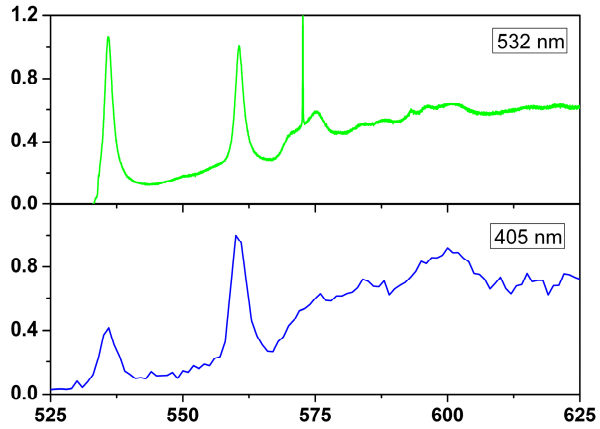


Fig. 2: Photoluminescence spectra acquired under 405 nm and 532 nm laser excitation wavelengths from the sample region irradiated with a $1\times10^{16}$ $cm^{-2}$ He fluence.

## CONCLUSIONS

In this work we reported the photo-excitation under 405 nm and 532 nm laser wavelengths of two sharp emission lines at 536.5 nm and 560.5 nm in He-implanted diamond. The correlation of the PL intensity with the implantation fluence indicates that these spectral features are related to complexes containing both He impurities and vacancies. These results provide promising perspectives on the fabrication of diamond color centers with appealing emission features. A future investigation of these luminescent centers at the single-photon emitter level could pave the way to appealing quantum optics applications.

## REFERENCES

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