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# Electrical control of deep NV centers in diamond by means of sub-superficial graphitic micro-electrodes

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## ABSTRACT

The control of the charge state of nitrogen-vacancy (NV) centers in diamond is of primary importance for the stabilization of their quantum-optical properties, in applications ranging from quantum sensing to quantum computing. In this work buried current-injecting graphitic micro-electrodes were fabricated in bulk diamond by means of a 6 MeV  $C^{3+}$  scanning micro-beam. The electrodes were exploited to control the variation in the relative population of the negative ( $NV^-$ ) and neutral ( $NV^0$ ) charge states of a sub-superficial NV centers ensemble located in the inter-electrode gap regions. Photoluminescence spectra exhibited an electrically-induced increase up to 40% in the  $NV^-$  population at the expense of the  $NV^0$  charge state, with a linear dependence from the injected current at applied biases smaller than 200V, and was interpreted as the result of electron trapping at

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NV sites. An abrupt current increase at  $\sim 300\text{V}$  bias resulted in a strong electroluminescence from the NV<sup>0</sup> centers, in addition to two spectrally sharp emission lines at 563.5 nm and 580 nm, not visible under optical excitation and attributed to self-interstitial defects. These results disclose new possibilities in the electrical control of the charge state of NV centers located in the diamond bulk, which are characterized by longer spin coherence times.

## 1 INTRODUCTION

The nitrogen-vacancy complex in diamond (NV center) emerged in the last decade as a prominent solid-state quantum system operating at room temperature, and has been exploited for innovative applications in quantum computing and quantum sensing [1-6]. Most of these applications heavily rely on the initialization, manipulation and readout of the spin state of the negatively charged (NV<sup>-</sup>) state of the defect. However, the NV center is affected by uncontrolled charge state instabilities [7], thus preventing a coherent spin manipulation of the NV<sup>-</sup> state before it accidentally converts to the NV<sup>0</sup> state [8].

In recent years, several works addressed the control of the charge state of the NV center by different approaches. The chemical stabilization of NV<sup>-</sup>/NV<sup>0</sup> charge state was investigated in shallow centers and nanodiamonds, by means of oxygen [9-11], fluorine [12] and hydrogen [13] surface termination. The NV charge state stability has been investigated as a function of laser power and wavelength excitation [7,14,15]. Furthermore, the electrical control was adopted to stabilize the negative charge state of shallow NV centers in a hydrogen-terminated sample [16,17], and to deterministically switch NV<sup>-</sup> centers to the neutral charge state through hole injection in p-i-n devices [18,19].

The charge state control of the NV<sup>-</sup> center by means of electrical pulse sequences is particularly appealing, since it would enable the development of integrated spintronic devices [18]. Despite the recent progresses, the current studies were mainly limited to surface (i.e.  $<14\text{ nm}$ ) defects [16,17] or to the stabilization of the NV<sup>0</sup> charge state [18,19], with the exception of the negative charge state

stabilization in p-i-n devices in a sandwich configuration [20]. On the other hand, the possibility of controlling deep  $NV^-$  centers in diamond using flexible electrode geometries would find useful applications in quantum metrology and quantum information processing, since deep sub-superficial  $NV^-$  centers are characterized by significantly longer spin coherence times due to the weaker interaction with surface defect states [21].

In this work, the electrical control of the charge state in NV ensembles is investigated in a single-crystal diamond substrate structured with sub-superficial graphitic micro-electrodes fabricated by means of MeV ion beam lithography [22]. The employed fabrication technique allows to define arbitrary electrode geometries with micrometric resolution in the diamond bulk (i.e. up to several micrometers below the sample surface) by exploiting the radiation-induced graphitization of the material occurring at the end of the MeV ion penetration range, and has already been successfully adopted to realize different integrated devices in diamond, such as bolometers [23,24], particle detectors [25], cellular biosensors [26,27] and IR emitters [28]. More pertinently to this work, sub-superficial graphitic electrodes were previously employed to stimulate electroluminescence from diamond color centers, both in multi-photon [29] and single-photon [30] emission regimes. Furthermore, the exploitation of the ion fabrication technique enabled to investigate the charge state conversion process by means of non-rectifying ohmic electrodes, thus taking advantage on the related charge injection mechanisms.

## 2 METHODS

### 2.1 Device fabrication

The employed sample was a  $3 \times 3 \times 0.3$  mm<sup>3</sup> single-crystal diamond substrate grown by ElementSix by CVD technique. This “optical grade” type IIa sample is characterized by nominal concentrations of substitutional nitrogen and boron of <1 ppm and <0.05 ppm, respectively. Two sub-superficial graphitic micro-electrodes were fabricated in the sample bulk by raster-scanning a focused

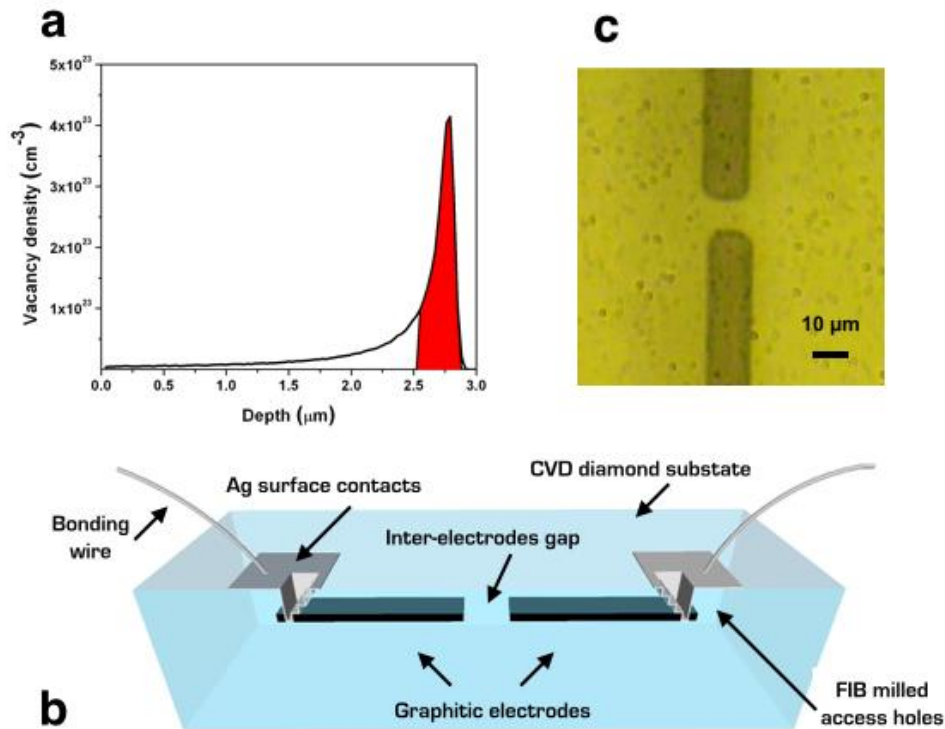
$\varnothing \sim 5 \mu\text{m}$  6 MeV  $\text{C}^{3+}$  beam along linear paths. The ion fluence ( $\sim 4 \times 10^{16} \text{cm}^{-2}$ ) was chosen to overcome the graphitization threshold [31] at the end of the ions range, i.e. at a depth of  $\sim 2.7 \mu\text{m}$  below the sample surface, as shown in **Figure 1a**.

The sample was subsequently annealed at 1000 °C in vacuum for 2 hours to convert the amorphized layer to a graphitic phase. This thermal process was concurrently exploited to induce the formation of a high-density ensemble of NV centers in the gap region comprised between the graphitic channels, due to the aggregation of native nitrogen atoms and the vacancies created by stray ions in the fabrication process. The concentration of induced NV centers in this region can be roughly estimated as follows. A native substitutional nitrogen concentration of  $10^{15} \text{cm}^{-3}$  was assumed from the manufacturer specification. The density of vacancies induced by the implantation of stray ions in the inter-electrodes gap during the fabrication process is estimated as of  $\sim 1 \times 10^{22} \text{cm}^{-3}$ . The “V + N  $\rightarrow$  NV” conversion efficiency is known to be in the 1-10% range [32]. So, the NV concentration could be estimated in the 10-100 centers  $\mu\text{m}^{-3}$  range. Such values are sufficiently high to prevent the observation of any non-classical feature in the light emission from NV centers, which were investigated as a purely classical ensemble of optically active centers.

Subsequently, the sample underwent a 30 min oxygen plasma treatment (20 sccm  $\text{O}_2$  flux, 30 W RF power, pressure  $2.5 \times 10^{-2}$  mbar) with the purpose of removing any residual surface conductivity associated with possible graphitization or contamination occurring during the thermal annealing. In addition, the plasma treatment ensured that the diamond surface was oxygen-terminated, and thus electrically insulating [33]. This feature enabled to investigate unambiguously the electrical conduction features of bulk diamond in the graphitic electrodes gap.

As schematically shown in **Figure 1b**, 30 keV  $\text{Ga}^+$  focused ion beam (FIB) milling was performed at the outer endpoints of the micro-channels to expose them to the sample surface. The FIB milling was followed by the deposition of 70 nm thick Ag contacts through a stencil mask, on which electrical connections to the external circuit were subsequently wire-bonded. The final device consisted

of two  $\sim 15 \mu\text{m}$  wide and  $\sim 100 \mu\text{m}$  long graphitic micro-electrodes spaced by a  $\sim 9 \mu\text{m}$  gap, as shown in **Figure 1c**.



**Figure 1:** Fabrication of sub-superficial graphitic electrodes in diamond. **a)** Vacancy-density depth profile induced by 6 MeV C<sup>3+</sup> ions implanted at a fluence of  $4 \times 10^{16} \text{ cm}^{-2}$ , as evaluated by SRIM2013.00 Monte Carlo code [34]. The vacancy density exceeds the graphitization threshold in the region highlighted in red, where graphitic electrodes are formed upon thermal annealing. **b)** Schematic representation of the device: the electrical connections of the graphitic electrodes to the external circuit are fabricated by FIB milling at their outer endpoints, in order to expose them to a subsequent Ag contact deposition and wire-bonding. **c)** Transmission optical micrograph of the inter-electrode gap region of the fabricated device.

## 2.2. Electrical and optical characterization

Two-terminal current-voltage (I-V) characteristics were measured with a standard setup (Keithley 6487 picoammeter/voltage source), both in dark conditions and under laser illumination. Increasing voltage steps of 2 V and a constant source time of 300 ms were adopted, both in the acquisition of the I-V curves and of the photoluminescence (PL) spectra from the biased device. The injected cur-

rent was measured during PL acquisitions to monitor the electrical stability of the device. PL measurements were performed on the inter-electrode gap region, under different bias conditions. The PL spectra were acquired with a Horiba Jobin Yvon HR800 Raman spectrometer equipped with a  $1800 \text{ mm}^{-1}$  diffraction grating ( $\sim 0.1 \text{ nm}$  spectral resolution). In all the experiments discussed in the following, photoexcitation was provided by a continuous 532 nm laser, with a power of 21.6 mW, as measured on the sample surface. A  $20\times$  air objective was employed to define a probed spot region of  $\sim 3 \mu\text{m}$  both in diameter and focal depth, i.e. comparable with the penetration range of 6 MeV  $\text{C}^{3+}$  ions in diamond, thus minimizing the effects of possible small stage drifts during the measurements at variable bias voltages. To account for slightly non-reproducible focusing conditions, all the reported PL spectra (as well as the combined PL/EL spectra reported in **Section 3.3**) were normalized to the intensity of the first-order Raman peak. Each PL acquisition from the biased device was followed by an acquisition at zero bias voltage, to both verify the absence of residual polarization effects and check the repeatability of the measurements. All measurements were performed in air in a controlled-temperature environment of  $20^\circ\text{C}$ .

### 3. RESULTS AND DISCUSSION

#### 3.1 Electrical characterization

##### *I-V characteristic in dark conditions*

The I-V characteristic of the device in dark conditions is reported in **Figure 2a** (black line). The current measured in these experimental conditions will be referred to as “dark current” in the following. At increasing bias between 0 V and 200 V, a quasi-linear increase of the dark current was observed, indicating an ohmic diamond-graphite interface with a typical resistance value of  $700 \text{ M}\Omega$  [22,35]. The I-V trend exhibited a moderate super-linear current increase at  $V_{bias} > 200 \text{ V}$ . As a critical bias voltage  $\sim 300 \text{ V}$  was reached, a sudden increase of the dark current was observed,



with currents larger than 10  $\mu\text{A}$  at 350 V. This behavior was interpreted in terms of Space-Charge-Limited Current (SCLC) caused by the injection of electrons at the ohmic contacts [36,37]. According to this model, the super-linear current increase observed at increasing voltage (i.e. in the 200–300 V range) is associated with the progressive filling of electron traps in the diamond band gap, while the abrupt current increase observed at  $V_{bias} > 300$  V indicates the complete filling of the available deep trap states. Such deviation from the ohmic conduction is well described, in the 200–280 V range, by the Mott-Gurney law (to guide the reader’s eye, the fitting line is superimposed in blue to the experimental data), describing a quadratic dependence on the applied bias typical of the space-charge-limited current model [37]. Assuming for simplicity a monoenergetical trap distribution in the diamond energy gap, the critical bias  $V_c = 300$  V represents the voltage at which the electron quasi-Fermi level overcomes the closest deep trap level  $E_t$  to the conduction band [37]. While the assumption of an individual type of electron trap in the band gap is rather simplistic, it is reasonable to assume that there is one predominant deep trap level which is responsible for the transition to the high-current-injection regime. The position of this level in the energy band gap was estimated according to the SCLC theory [37], as described below.

Firstly, the following equation expresses the higher threshold value  $V_c = 300$  V:

$$(1) \quad V_c = q N_t d^2 / (2 \varepsilon_0 \varepsilon_r)$$

where  $q$  is the elementary charge,  $N_t$  is the trap density,  $d = 9 \mu\text{m}$  is the width of the inter-electrode gap region,  $\varepsilon_r = 5.5$  is the dielectric permittivity of diamond and  $\varepsilon_0$  is the vacuum permittivity. From Eq. (1), a  $N_t = (2.2 \pm 0.3) \times 10^{15} \text{ cm}^{-3}$  value was derived. Considering the  $\varnothing \sim 5 \mu\text{m}$  spot size of the 6 MeV  $\text{C}^{3+}$  micro-beam adopted for the device fabrication, the implantation of stray ions with a fluence smaller than one order of magnitude in the inter-electrode region is expected [29]. Thus it is reasonable to ascribe the trap density to the residual concentration of ion-induced defects in the active region of the device after the thermal treatment.

Moreover, the following formula expresses the lower threshold voltage  $V_{tr} = 200$  V, where a deviation from the linear ohmic conduction becomes apparent [37]:

$$(2) \quad V_{tr} = 8/9 \cdot (q n_0 d^2) / (\epsilon_0 \epsilon_r \theta)$$

where  $n_0 = 8.1 \times 10^9 \text{ cm}^{-3}$  is the free electron concentration at thermal equilibrium as estimated from the resistivity (evaluated assuming a 15  $\mu\text{m}$  wide and 3  $\mu\text{m}$  thick active region of the device) of the device at low voltages assuming an electron mobility of  $\mu = 2200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  [25], and  $\theta$  is the ratio between free and trapped electrons when the electron quasi-Fermi level lies below the trap energy  $E_t$  [37]. From Eq. (2), a value of  $\theta = 9.6 \times 10^{-6}$ , namely the fraction of the total charge density at the anode which is available for conduction at biases lower than  $V_{tr}$  [36], was obtained.

Finally, the following formula expresses the  $\theta$  value [36,37]:

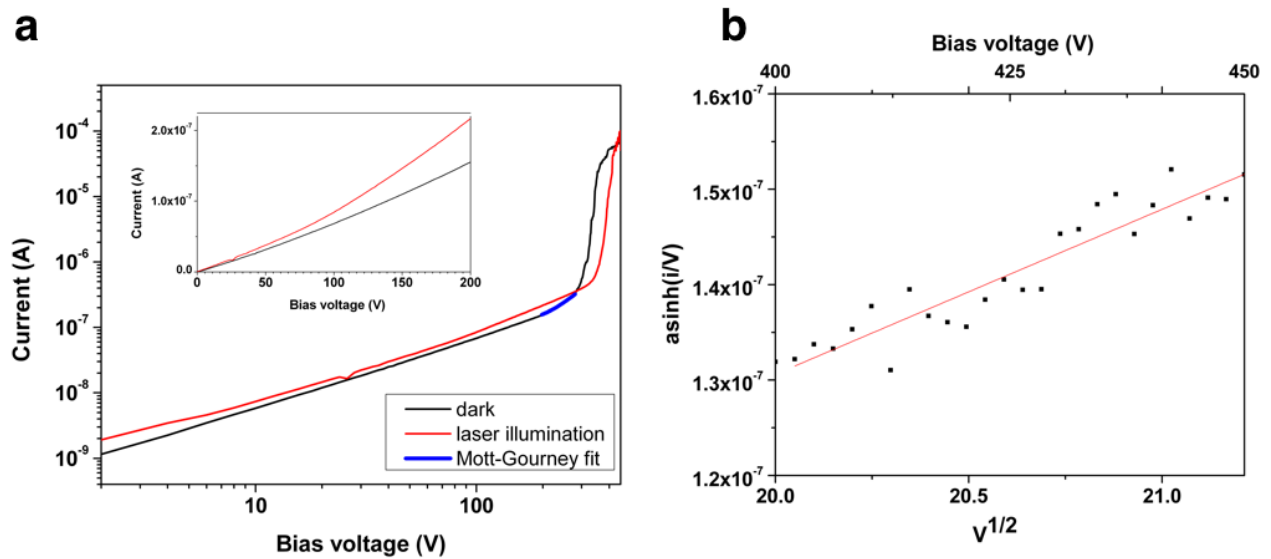
$$(3) \quad \theta = N_c / g N_t \cdot \exp(-\Delta E_t / kT)$$

where  $N_c = 1 \times 10^{20} \text{ cm}^{-3}$  is the effective density of states in the conduction band,  $g$  is the degeneracy of the trap level,  $\Delta E_t$  is the difference between the energy corresponding to the bottom of the conduction band and the energy of the trap level,  $k$  is the Boltzmann constant and  $T$  is the temperature. From Eq. (3), a  $\Delta E_t = 0.56 \text{ eV}$  was obtained under the assumption of  $g = 2$  (see below) and room temperature conditions (i.e. neglecting any possible contribution from Joule heating). Indeed, such  $\Delta E_t$  value is in reasonable agreement with the position of the excited state of the  $\text{NV}^-$  center, i.e. 0.6 eV from the bottom of the conduction band [38]. On the other hand, also the assumed  $g = 2$  value is compatible with the excited state of the  $\text{NV}^-$  center [39]. Thus, we conclude that the electron quasi-Fermi energy at the critical threshold  $V_c$  overcomes the excited state of the  $\text{NV}^-$  center, so that all  $\text{NV}^-$  centers (and all deeper levels in the band gap) are filled. Consequently, the SCLC model suggests that an almost complete conversion by electron capture from the neutral to the negative charge state of the NV center is achieved at  $V_{bias} = V_c$  (see below for a more detailed discussion).

The I-V trend in high-current-injection regime (i.e., at  $V_{bias} > 400$  V) is suitably described with a Poole-Frenkel (PF) model [40], as demonstrated by the linearization of the “ $\text{asinh}(i/V)$  vs  $V^{1/2}$ ” trend (see **Figure 2b**) deriving from the characteristic PF expression  $I \propto V \sinh(aV^{1/2}/kT)$  [41], in good agreement with previous findings on similar diamond devices [30]. According to this model, the conduction mechanism is dominated by the thermally induced electron emission from traps into the conduction band under the effect of the strong applied electric field [37]. Such exponential dependence of the current from the applied bias could hide the quadratic dependence of the SCLC conduction mechanism, which is however interpreted as the cause of the abrupt current injection in the active region of the device. The appearance of a temperature-related current contribution can indeed be regarded as a consequence of the high current density in the small inter-electrode gap. Concurrently to the transition to this high-current-injection regime, an intense electroluminescence (EL) emission was observed from the inter-electrode gap region. More details on this effect and the above-mentioned interpretation are reported in **Section 3.3**.

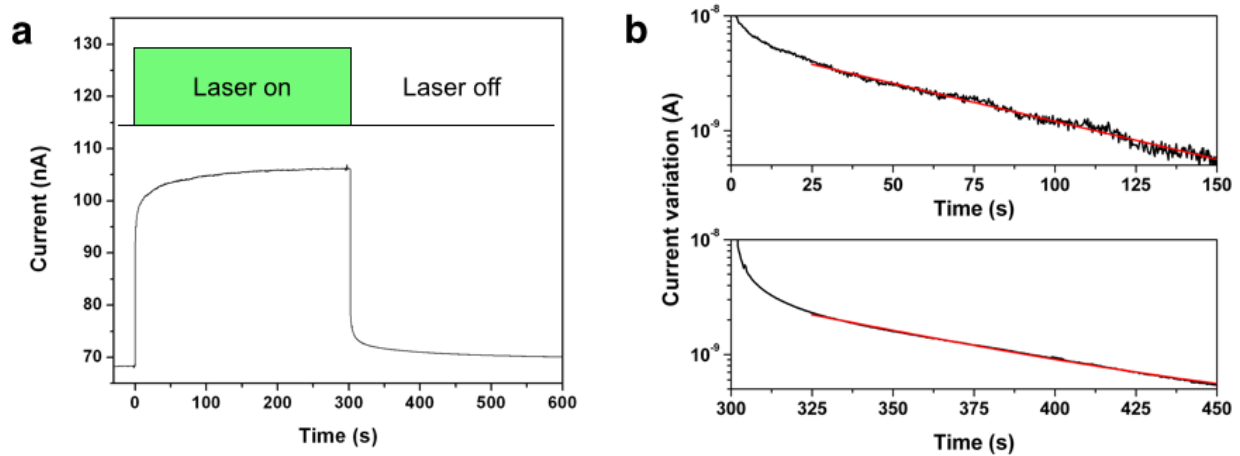
#### *I-V characteristics under laser illumination*

I-V curves were also acquired under laser illumination of the inter-electrode gap region of the device (**Figure 2**, red line) with the same experimental parameters. The current measured in these conditions will be referred to as “total current”, as it consists of a further contribution (“photocurrent” in the following) arising from photo-generated carriers. A quasi-linear trend in the I-V curve was observed at low bias voltages ( $<100$  V), while a super-linear increase of the total current was apparent at higher voltages. At bias voltages smaller than  $V_c$ , the  $\sim 50\%$  current increase under laser illumination indicates that the optical excitation promotes the de-trapping of carriers.



**Figure 2:** **a)** I-V characteristic in dark conditions (black line) and under laser illumination (red line) of the inter-electrode gap region. In the inset the data are plotted in linear scale in the 0-200 V range for sake of readability. The blue line, representing the quadratic fit of the dark I-V characteristic in the 200-280V range, evidences that the curve follows the Mott-Gourney law. **b)** PF electrical conduction in high-current-injection regime. On the basis of the PF formula  $I \propto V \sinh(aV^{1/2}/kT)$ , the data in the 400-450V range are linearized by suitably re-scaling the quantities reported on the axes.

Moreover, upon laser illumination the transition to a high-current-injection regime was shifted at a higher threshold voltage ( $\sim 350$  V). This evidence indicates that the optically-induced detrapping of the carriers represents a competing process with respect to the electron trap filling in the interelectrode gap, thus supporting the above-mentioned interpretation of the transition between low- and high-current-injection regimes based on the SCLC process.



**Figure 3:** **a)** Total current chronogram under variable laser illumination of the inter-electrode gap region, at an applied bias voltage of 100 V. As schematically shown in the inset, the laser illumination is turned on at time  $t = 0$  s and switched off after 300 s. **b)** Chronograms of the absolute value of the difference between the measured current and the asymptotic baseline (black lines) in correspondence of the laser turn-on (top) and subsequent switch-off (bottom) together with the corresponding exponential fits (red lines).

The carriers trapping/detrapping mechanisms were further investigated with current measurements under variable laser illumination. As shown in the chronogram reported in **Figure 3a**, the current in the device biased at 100 V was sampled in concurrence with the turning on and the switching off of the laser illumination, to investigate the related characteristic trapping/detrapping times.

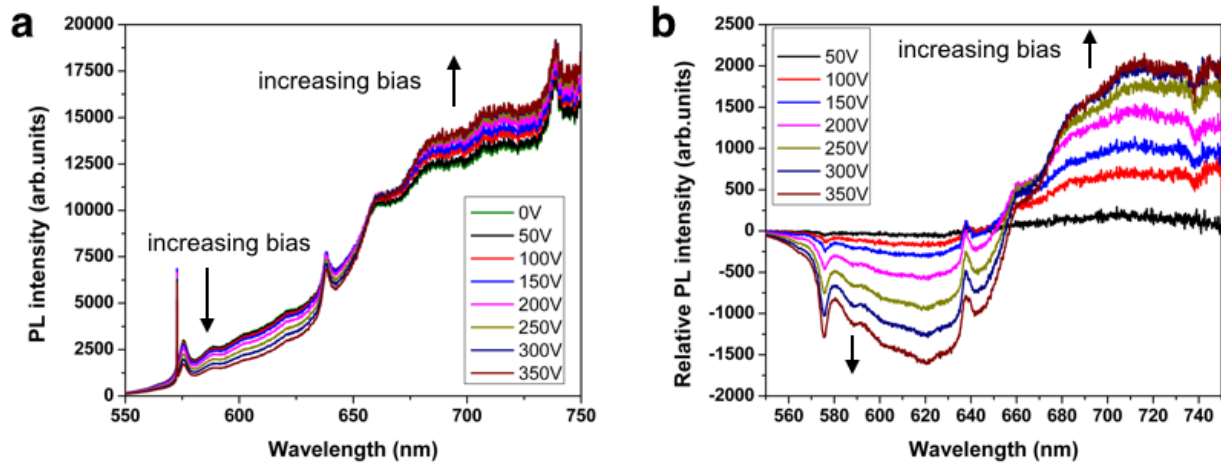
As shown in **Figure 3b**, both the transitions were characterized by the sum of a fast exponential term and a slower one. In both cases, the former term was associated with a characteristic time smaller than the sampling period (i.e. 300 ms). We ascribed this first component to the trapping/detrapping of shallower defects. The slower components of the turn-on and switch-off current transients were characterized by significantly longer decay times, i.e.  $(65.6 \pm 0.4)$  s and  $(69.8 \pm 0.7)$  s, respectively. We ascribed this second component to the trapping/detrapping of deep defects in the band gap. These trapping/detrapping effects can be associated with the photo-induced conversion of the charge state of the probed NV centers [14,42], although the possible contribution of other deep levels associated with different defects cannot be ruled out. Temperature-dependent

photocurrent measurements could indeed be useful to further elucidate this issue. It is however worth noting that the measured characteristic PL decay times are significantly shorter than what recently reported for trapping/detrapping of the P1 center (i.e. substitutional nitrogen defects) in photoconducting diamond [43], so that at least this possible attribution can be ruled out.

### 3.2 Charge state conversion

The PL emission from the inter-electrode gap region of the device was measured under different applied bias voltages, with the purpose of assessing the variation of the photophysical properties of the probed NV centers as a function of the injected current between the electrodes. In **Figure 4a** the PL spectrum from the unbiased device is reported together with PL spectra acquired at increasing bias voltages in the 0–350 V range, i.e. below the transition to the high-current-injection regime (and the concurrent EL emission) is observed. The spectra exhibit the typical PL features of an “optical grade” diamond sample after low-fluence ion irradiation and subsequent annealing, such as the intense first-order Raman peak at 572 nm (corresponding to a  $1332\text{ cm}^{-1}$  Raman shift), and the  $\text{NV}^0$  and  $\text{NV}^-$  zero phonon lines (ZPLs) at 575 nm and 638 nm, respectively, together with their associated phonon sidebands at higher wavelengths [8]. Additionally, the luminescence peak at 740 nm is attributed to residual GR1 centers, i.e. to neutral isolated vacancies [44]. A systematic variation of the relative intensities of the PL features associated with the different NV charge states is clearly visible. For sake of readability, in **Figure 4b** we report the “relative” PL spectra acquired from the biased device, i.e. after the subtraction of the reference PL spectrum acquired at zero bias. The most apparent feature of the data displayed in **Figure 4b** is a substantial decrease in the  $\text{NV}^0$  emission at increasing bias, concurrently to an increase in the  $\text{NV}^-$  emission. It is worth noting that the apparent decrease in the  $\text{NV}^-$  ZPL emission is due to the large decrease of the background represented by the  $\text{NV}^0$  phonon sideband, which results in a lowering of the  $\text{NV}^-$  ZPL peak baseline. If the above-mentioned background is subtracted, the intensity of the  $\text{NV}^-$  ZPL actually increases with the applied bias, as indicated by the increasing local maximum observed at  $\lambda = 638\text{ nm}$ , and confirmed by

the visible increase in intensity of the  $NV^-$  phonon sideband at higher wavelengths. It is also worth noting that, similarly to the  $NV^0$  emission, the GR1 luminescence peak decreases at increasing biases, as indicated by the deepening dip at 740 nm.



**Figure 4:** a) PL spectra acquired from the inter-electrode gap region at increasing applied bias voltages. b) Relative PL spectra acquired from the biased sample, after subtraction of the reference PL spectrum acquired from the unbiased device.

The quantities  $A_0(i)$  and  $A_-(i)$  are defined as the values of the integrals of the PL counts calculated respectively in the 572-580 nm ( $NV^0$  ZPL) and 634-642 nm ( $NV^-$  ZPL) spectral intervals. Such values are expressed as functions of the total injected current  $i$  and were estimated after the subtraction of their respective baselines. The  $A_0(i)$  and  $A_-(i)$  values were then normalized to their respective reference values acquired from the unbiased device, and the resulting  $A_0(i)/A_0(0)$  and  $A_-(i)/A_-(0)$  normalized values are reported in **Figure 5a** as a function of the corresponding injected current. A relative uncertainty of 5% on the ZPL integrals was estimated.

The data reported in **Figure 5a** exhibit increasing and decreasing linear trends, respectively for the  $NV^-$  (black square dots) and  $NV^0$  (red circular dots) normalized ZPL emissions. A quantitative evaluation of the relative concentrations of NV centers in different charge states was performed under the assumption that the current-dependent local concentrations of  $NV^0$  and  $NV^-$  centers in the

probed region, denoted as  $n_0(i)$  and  $n_-(i)$ , are directly proportional to the correspondent ZPL intensity  $A_{0/-}(i)$ . Thus it follows that:

$$(4) \quad n_{0/-}(i) / n_{0/-}(0) = A_{0/-}(i) / A_{0/-}(0)$$

where the the “0/-” subscript refers alternatively to either of the two NV charge states.

Furthermore, we assumed that the probed NV centers only change their charge states between the  $NV^0$  and  $NV^-$  ones, i.e. that a possible (and yet to be conclusively demonstrated) population fraction of “dark”  $NV^+$  centers remains (if at all present) unchanged under various injection conditions. Such hypothesis is qualitatively supported by the presence of a quasi-isosbestic point in the PL spectra at  $\sim 655$  nm (**Figure 4b**), at which the emission intensity remains unchanged at increasing voltages. This observation is in agreement with the lack of conversion from  $NV^0$  and  $NV^-$  to an optically-inactive NV charge state, whose concentration remains unchanged (if not zero) at all electrical biases. Under these assumptions, it follows that the sum of the overall population of  $NV^-$  and  $NV^0$  centers ( $n_-(i)$  and  $n_0(i)$ , respectively), is constant for any current flowing in the device:

$$(5) \quad n_-(i) + n_0(i) = n_{\text{tot}}$$

From the linear fitting in the 0–405 nA range of the “ $n_{0/-}(i)/n_{0/-}(0)$  vs  $i$ ” data reported in **Figure 5a** it is possible to express each NV charge state concentration as follows:

$$(6) \quad n_{0/-}(i) = n_{0/-}(0) \cdot (1 + k_{0/-} \cdot i)$$

where  $k_0 = (-0.99 \pm 0.03) \mu\text{A}^{-1}$  and  $k_- = (+1.06 \pm 0.06) \mu\text{A}^{-1}$  are the respective linear coefficients.

From Eqs. (5) and (6) it is possible to obtain, for the unbiased device:

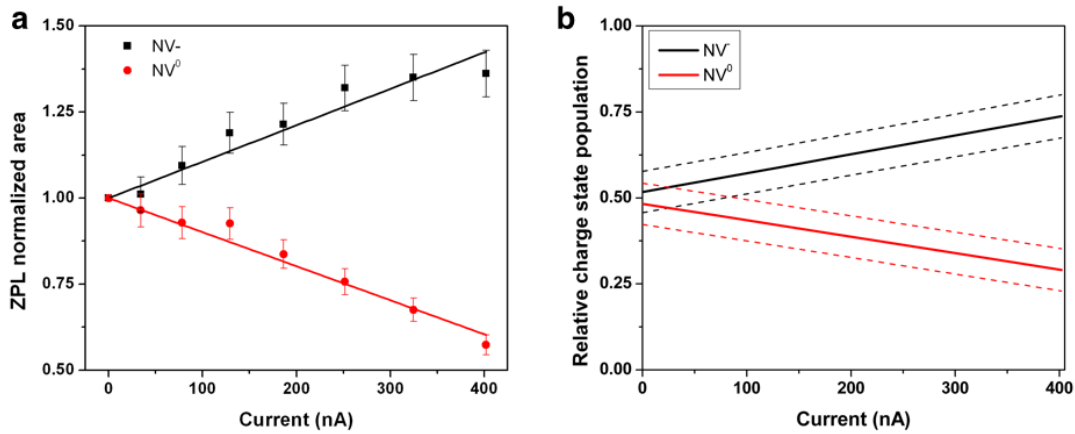


$$(7) \quad n_{-}(0) / n_{0}(0) = |k_{0} / k_{-}$$

It follows that  $n_{-}(0) / n_{tot} = (0.52 \pm 0.06)$  and  $n_{0}(0) / n_{tot} = (0.48 \pm 0.06)$ . From these values and the previously derived linear coefficients it is possible to obtain the relative concentrations of the different NV charge states as a function of the injected current (see **Figure 5b**):

$$(8) \quad n_{0}(i) / n_{tot} = (0.48 \pm 0.06) - (0.48 \pm 0.07) \cdot i [\mu A]$$

$$n_{-}(i) / n_{tot} = (0.52 \pm 0.06) + (0.55 \pm 0.08) \cdot i [\mu A]$$



**Figure 5:** **a)** Normalized ZPL intensity from NV<sup>-</sup> ( $A_{-}(i)/A_{-}(0)$ , black square dots) and NV<sup>0</sup> ( $A_{0}(i)/A_{0}(0)$ , red circular dots) centers as a function of the total injected current  $i$ . Linear fitting curves of the data in the 0-405 nA range are reported by the continuous lines. **b)** Variation of  $n_{-}(i)/n_{tot}$  (black line) and  $n_{0}(i)/n_{tot}$  (red line) as a function of the total injected current  $i$ , as resulting from **Eq. (8)**. The dashed lines indicate the uncertainty associated to our estimation, as derived from the fitting procedure.

It is worth noting that a relative concentration of NV<sup>-</sup> centers of  $n_{-}/n_{tot} = (0.74 \pm 0.09)$  is achieved just below the critical threshold (350 V, ~ 400 nA injected current). Such concentration corresponds to a ~40% increase with respect to the unbiased device. Considering that the steady-state NV<sup>-</sup> relative population  $n_{-}/n_{tot}$  is always smaller than 0.75 under non-resonant excitation [38], this result indicates that the maximum conversion to the negative charge state under electrical control is

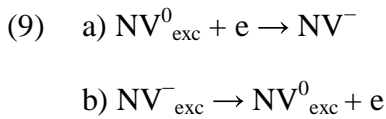
achieved. It is worth remarking that this maximum value is observed in correspondence of the transition to the high-current-injection regime (red curve in **Figure 2**).

This evidence further supports the interpretation of the charge transport in the device in terms of the SCLC model discussed in **Section 3.1**. According to this interpretation, the electron trapping occurring at the NV centers causes their progressive conversion to the negative charge state; the transition to a high-current-injection regime then occurs once all the trap levels are filled. Such interpretation is reinforced by the decrease, at increasing voltages, of the GR1 PL emission associated with the neutral vacancy. It is worth noting that such a decrease could be similarly ascribed to the conversion, upon electron trapping, of the vacancy to the negative charge state, which is not optically active under 532 nm laser excitation [44].

On the other hand, an alternative explanation of the change of the NV charge state based on a variation in the surface electric potential can be ruled out, since a bulk region is probed by means of sub-superficial electrodes. Moreover, it should also be considered that the sample surface was oxidized during the fabrication process to achieve its electrical insulation. While this feature partly contributes to promote the NV negative charge state for the unbiased device [9-11], it however allows to rule out any voltage-dependent chemically-induced shift of the Fermi level occurring below the surface of H-terminated diamond [16,17], which is due to electrically-dependent band bending and thus results in the charge state conversion of superficial (i.e. few tens of nm) NV centers. In this way, the electrical control of the  $NV^-$  charge state can be unambiguously attributed to electrical conduction mechanisms occurring exclusively in bulk diamond.

Furthermore, since the injection of a hole current promotes the conversion of the NV centers population to the neutral charge state [18], electron trapping/detrapping from/to the conduction band is identified as the predominant process. The occurring of hole trapping/detrapping events cannot be ruled out, but a minority contribution from these processes is expected. This interpretation is based on a unipolar charge transport, and is supported by previous independent experimental results ob-

tained from “Ion Beam Induced Charge” (IBIC) measurements, where a predominant electron contribution to the charge transport properties was observed in the same type of diamond devices [45]. The proposed trapping/detrapping processes associated with electrically-induced NV charge state conversion are: the capture of an electron by an  $NV^0$  center resulting in the formation of an  $NV^-$  state [46] and, conversely, the detrapping of one electron from the  $NV^-$  center to the conduction band, upon either electrical or optical excitation, leading to a switching to the neutral  $NV^0$  state [18,38,42]:



Consistently with what reported in [14,42], we assume that the electron trapping/detrapping mainly occurs at the excited states (labeled as  $NV_{\text{exc}}^-$  and  $NV_{\text{exc}}^0$  in **Eq. 9**) of the two types of center, due to their closer proximity to the conduction band edge with respect to their respective ground states. In agreement with what discussed in previous works [11,16], the relative increase in the  $NV^-$  concentration originates from a shift in the electron quasi-Fermi level, due to the progressive filling of trap states in the band-gap at increasing currents. As highlighted by the electrical characterization discussed in **Sect. 3.1**, the transition to a high-current regime occurs when the electron quasi-Fermi level reaches the relevant trap state placed at 0.56 eV below the conduction band. Such transition indicates that a complete filling of all the deeper level in the band gap is achieved, including the conversion of the NV centers to the negative charge state by electron capture.

A schematic representation of the concurring electron trapping/detrapping processes responsible for the NV charge state modification in low-current-injection regime is reported in **Figure 6**. In the figure, the green band represents an excitation energy corresponding to the 532 nm laser from the conduction band. The electronic transitions of interest are highlighted in green or blue, respectively for trapping and detrapping processes.

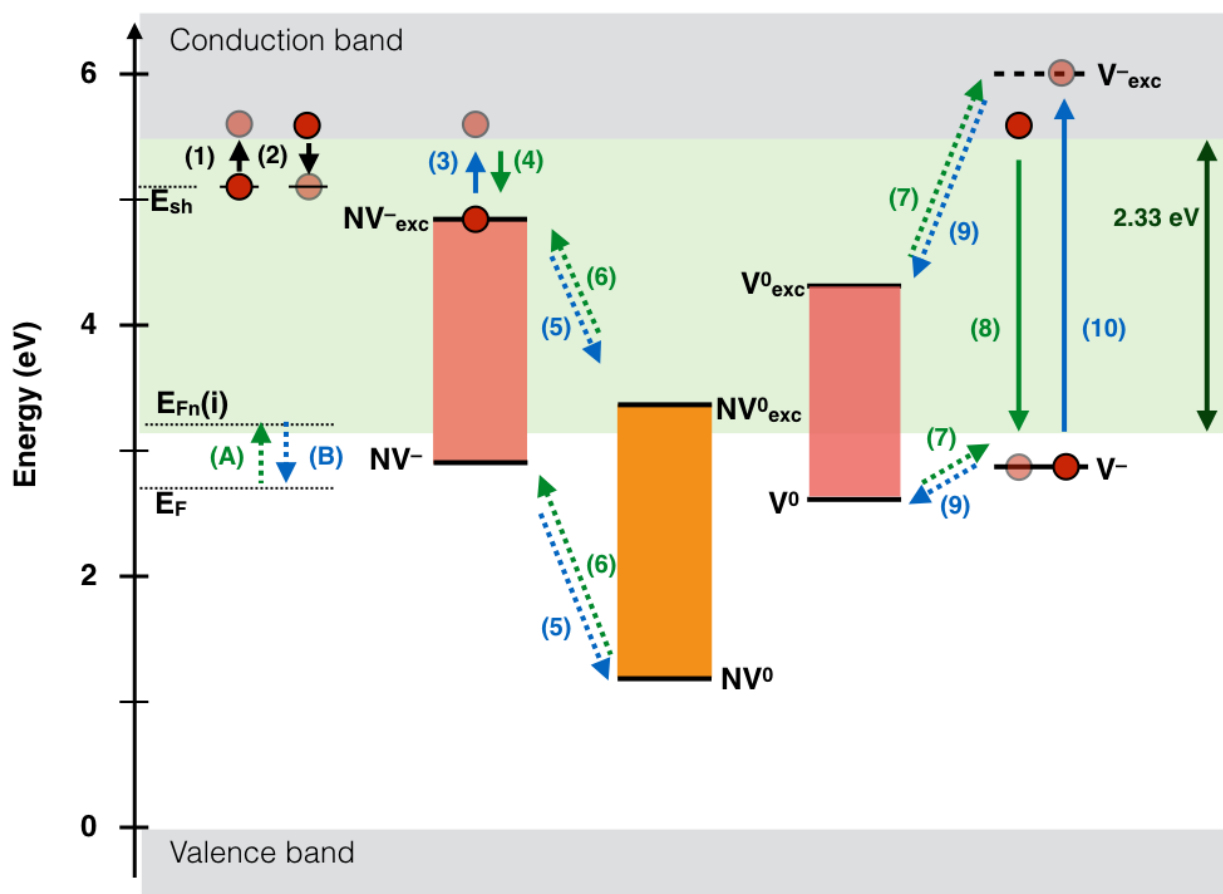
The diagram represents the energy levels of the ground and excited states of the  $NV^-$  and  $NV^0$  centers [8]. In the following, the position of all energy levels is intended as an energy difference from the conduction band. The ground states of the  $NV^-$  and  $NV^0$  centers are located at 2.54 eV and 4.3 eV, respectively [16,38]; similarly, the corresponding excited states  $NV^-_{exc}$  and  $NV^0_{exc}$  lay at 0.6 eV and 2.14 eV [16]. The ground ( $V^0$ , 2.86 eV) and excited ( $V^0_{exc}$ , 1.18 eV) states of the GR1 center, i.e. the neutral single vacancy are also reported [39]. The negatively charged vacancy  $V^-$  (corresponding to the ND1 luminescent center) has a ground state placed at 2.6 eV; its excited state  $V^-_{exc}$  (3.15 eV above the ground state) lays within the conduction band [44].

The following electronic transitions are proposed to play a key role in the charge state modification of the vacancy and of the nitrogen-vacancy center. The conduction of carriers injected at the ohmic diamond/graphite interface occurs mainly within the conduction band. In addition, trapping/detrapping phenomena (labeled as “1-4” and “8, 10” in **Figure 6**) may occur, involving transitions to/from the energy levels of the defects from/to the conduction band. The considered detrapping/trapping processes can involve shallow traps laying at energy  $E_{sh}$  (labeled as “1” and “2” in **Figure 6**), the excited state of  $NV^-$  centers labeled as “3”/“4”, as described by **Eq. (9)**, or the ground state of negative vacancies (labels “10”/“8”, respectively).

The electron detrapping from the  $NV^-$  center results in its conversion to the  $NV^0$  state [15] (labeled as the blue dashed arrows “5” in **Figure 6**). Conversely, the transition of the  $NV^0$  to the negative charge state  $NV^-$  (labeled as the green dashed arrows “6” in **Figure 6**) is assumed to follow an electron trapping from the conduction band to the available energy level at 0.56 eV, corresponding to the  $NV^-_{exc}$  excited state (transition labeled as “4” in **Figure 6**).

At increasing electron currents, the progressive filling of the trap states available in the band gap results in an increase in the electron quasi-Fermi level  $E_{Fn}(i)$  (labeled as the green dashed arrow “A” in **Figure 6**): the  $NV^-$  charge state is then the most favored. Conversely, at decreasing injected currents the electron quasi-Fermi level decreases upon electron detrapping (labeled as the blue dashed arrow “B” in **Figure 6**), thus increasing the  $NV^0$  population.

Similarly, the decrease in the PL intensity of the GR1 center at increasing currents is interpreted as due to the conversion (labeled as the green dashed line “7” in **Figure 6**) of the neutral vacancy to the negative charge state. This process, in turn, is a consequence of the non-radiative electron trapping from the band gap to the  $V^-$  ground state (green line “8” in **Figure 6**). The inverse charge state conversion is presented for completeness (dashed blue line “9” in **Figure 6**) as the result of an electron transition from the  $V^-$  ground state to the conduction band, where its excited state lays (labeled as the blue arrow “10” in **Figure 6**).



**Figure 6:** The region highlighted in green indicates the energy levels, which can be optically detrapped upon 532 nm laser excitation (2.33 eV). Schematic representation (in scale) of the electron trapping/detrapping mechanisms occurring in the inter-electrode gap region. Detrapping (labeled as “1”) and trapping (labeled as “2”) from/to shallow trap levels at a generic energy  $E_{sh}$  contribute to the measured photocurrent (see **Figure 3**). Electron detrapping (blue line, labeled as “3”) from an excited  $NV^-$  center results in the conversion to its

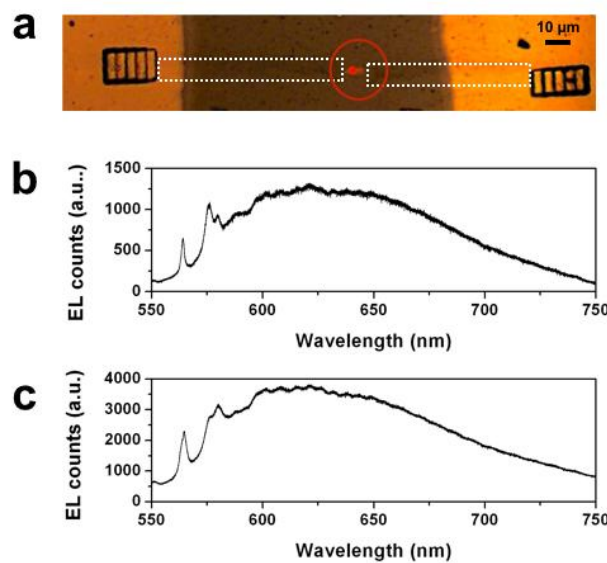
neutral charge state (blue dashed line, labeled as “5”). Conversely, electron trapping at the  $NV_{exc}^-$  level (green line, labeled as “4”) causes the conversion of the  $NV^0$  center to its negative charge state (green dashed line, labeled as “6”). Similarly, an electron trapping to (green arrow, label “8”) or detrapping from (blue arrow, label “10”) the ground state of the negative vacancy results respectively in the  $V^0 \rightarrow V^-$  (blue dashed line, labeled as “7”) or  $V^- \rightarrow V^0$  conversion (green dashed line, labeled as “9”), respectively.

### 3.3 Electroluminescence

The study of the electrically controlled charge state conversion was limited by the transition to a high-current-injection regime observed at bias voltages higher than 350 V (see **Figure 3a**). This transition was fully reproducible and stable over multiple excitation cycles. A non-negligible electrically induced luminescence was detectable for injected currents larger than 10  $\mu$ A, i.e. above the transition to the high-current-injection regime, while no EL emission could be detected at lower currents within the experimental sensitivity.

EL was investigated at increasing bias voltages under no laser illumination. An optical micrograph acquired at a bias voltage of 500 V is shown in **Figure 7a**, exhibiting an intense red emission visible by naked eye in the inter-electrode gap region. EL spectra acquired at 350 V and 500 V bias voltage with the same light collection setup adopted for PL measurements are reported in **Figures 7b** and **7c**, respectively. The main spectral feature is the emission from the  $NV^0$  center, which is clearly characterized by the ZPL at 575 nm and its phonon sidebands at higher wavelengths. The  $NV^-$  emission component is absent from the EL spectrum, consistently with previous reports of the absence of such emission under electrical excitation [19,44]. Moreover, two sharp EL emission lines (not active under optical excitation at 532 nm), are clearly visible at  $\lambda = 563.5$  nm and  $\lambda = 580$  nm. As shown in **Figures 7b** and **7c**, at increasing injected currents the two above-mentioned EL lines display a similar increase in emission intensity, which is more pronounced with respect to the  $NV^0$  emission. Indeed, the  $NV^0$  ZPL line is barely distinguishable at 500 V bias (see **Figure 7c**). The strong correlation between the emission intensities of the  $\lambda = 563.5$  nm and

$\lambda = 580$  nm lines suggests a possible attribution to the same defect family or to different charge states of the same complex. Although an exhaustive investigation of these previously unreported EL emission lines goes beyond the scope of the present work, they are tentatively attributed to self-interstitial defects, i.e. pairs of nearby interstitial atoms along the  $\langle 100 \rangle$  axis, consistently with what was previously observed in cathodoluminescence and photoluminescence under 488 nm laser excitation, in ion- and electron-irradiated diamonds [44,47].



**Figure 7:** **a)** Reflection optical micrograph of the device biased at a voltage of 500 V. The edges of the (otherwise barely visible) graphitic electrodes are highlighted by the white dashed line for sake of clarity. An intense EL emission (circled in red) is clearly visible as the red spot in the inter-electrode gap region. **b)** EL spectrum acquired from the inter-electrode gap region at a bias voltage of 350 V. **c)** EL spectrum acquired from the same region at a bias voltage of 500 V.

A quantitative analysis of the EL emission intensity as a function of the injected current was limited by the strong spectral overlap of the  $\text{NV}^0$  ZPL with the 580 nm emission line. Furthermore, any indication on the NV charge state conversion was prevented by the absence of  $\text{NV}^-$  emission in EL regime. However, a qualitative analysis of the process was possible by a PL investigation of the device in high-current-injection regime, i.e. at bias voltages higher than 400 V under laser illumina-

tion. In this case, the luminescence spectra acquired in the inter-electrode gap region included both a PL and an EL contribution. The former contribution was associated to the optical excitation of  $NV^0$ ,  $NV^-$  and GR1 centers, while the latter one consisted in the  $NV^0$  spectral component and the two afore-mentioned interstitial-related emissions. **Figure 8a** shows such combined “PL+EL” spectra acquired at increasing bias voltages (400 V, 450 V and 500 V), while also reporting for comparison a PL-only emission spectrum acquired from the unbiased device.

At increasing bias voltages, the PL+EL spectra exhibit an increase in the emission intensity over the whole spectral range. The corresponding injected current values can be found in **Figure 2a** (red curve). Similarly to what reported in **Figure 4b**, for sake of readability **Figure 8b** shows the “relative” PL+EL spectra obtained after subtraction of the reference spectrum collected from the unbiased device.

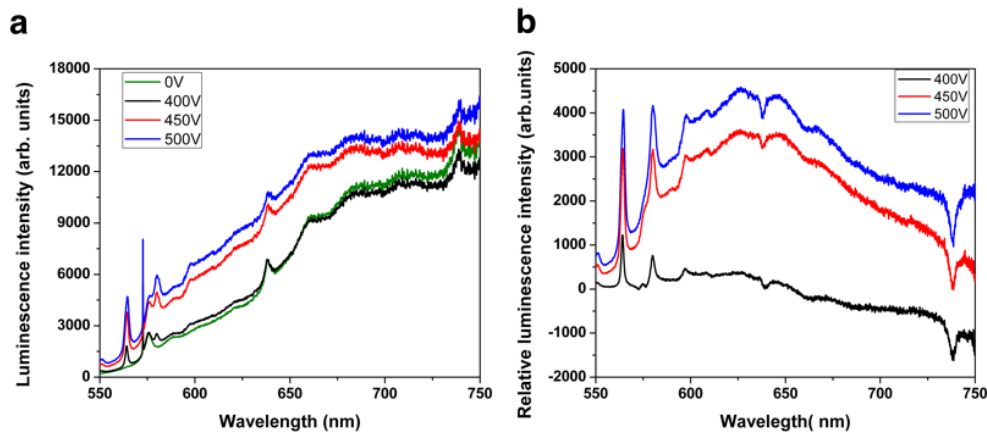
Firstly, the significant increase in emission intensity from the interstitial-related emission lines at 563.5 nm and 580 nm at increasing bias voltages is clearly visible. On the other hand, as previously mentioned the increase in the  $NV^0$  emission is significantly less pronounced with respect to the two afore-mentioned peaks. Nevertheless, a non-negligible increase in the  $NV^0$  emission can be appreciated by considering the increase in its phonon sidebands. While the overall increase in  $NV^0$  emission at increasing injected currents arises in large part from the progressive increase of EL emission (see **Figures 7b** and **7c**), it cannot be ruled out that the  $NV^-_{exc} \rightarrow NV^0_{exc} + e$  conversion process is also favored by the underlying electrical conduction mechanism.

On the other hand, the deepening local minimum at  $\lambda = 638$  nm indicates that the intensity of the  $NV^-$  emission (and thus the  $NV^-$  centers concentration) decreases at increasing bias voltages in the high-current-injection regime. Remarkably, this trend is opposite to what was observed at bias voltages below the critical threshold of 350 V, i.e. a progressive increase in the  $NV^-$  charge state concentration at increasing voltages (see **Figure 4b**). It is interesting to notice that such behavior is the same as reported in the study of the charge-state conversion process of NV centers in p-i-n devices



in forward bias [20]. In that case, however, the charge state conversion at biases smaller than the built-in voltage was interpreted in terms of a pure bending of the energy bands.

Finally, it is worth remarking that a significant decrease in the  $V^0$  emission is still observed at increasing biases, as confirmed by the deepening local minimum observed at  $\lambda = 740$  nm. Differently from what observed for the  $NV^-$  emission, this effect is in line with the same trend observed in low current-injection regime (see **Figure 4b**).



**Figure 8:** **a)** PL+EL spectra acquired under laser excitation at increasing bias voltage in the high-current-injection regime ( $V_{\text{bias}} = 400\text{-}500$  V). The PL spectrum acquired from the unbiased device (green line) is also reported for comparison. **b)** Corresponding relative luminescence spectra obtained after subtraction of the reference PL spectrum acquired at zero bias.

The observation of EL in a high-current-injection regime dominated by a Poole-Frenkel conduction is somewhat surprising, since the EL emission was previously demonstrated in p-i-n devices to be correlated with electron-hole recombination processes at NV sites, originating from double carriers injection at the electrodes [19,48]. While a hole injection in low-current regime could not be ruled out in first instance, the results discussed in **Section 3.2**, combined with the previous findings on NV conversion to the neutral charge state upon hole capture [18], indicate a net contribution to the modification of charge state of the nitrogen-vacancy center which is ascribable to a majority electron current [18], an interpretation which is fully consistent with previous independent experimental results obtained from “Ion Beam Induced Charge” (IBIC) measurements in similar devices [45].

On the other hand, the increasing conversion to the  $NV^0$  charge state at increasing bias suggests that the transition to a high-current regime involves the injection of a significantly higher density of holes in the inter-electrodes gap, with respect to the low-current behavior. This interpretation is consistent with previous reports [19,48] on the observation of EL emission in presence of a non-negligible hole component in the high current-injection regime.

Finally, it is worth mentioning that, on the basis of the present results, an interpretation of the obtained results in high-current regime exclusively based on a thermally-stimulated trapping/detrapping process consistent with the Poole-Frenkel conduction mechanism cannot be ruled out. In this latter interpretation, a high rate detrapping, combined with a high pump electron current can in principle fulfill the same role as the electron-hole injection and recombination in the electrical stimulation of the  $NV^0$  emission.

#### 4. SUMMARY AND CONCLUSIONS

In this work, we demonstrated that sub-superficial graphitic electrodes can effectively be exploited to control the charge state of nitrogen-vacancy complexes in diamond. The electrical characterization of the device highlighted an ohmic conduction mechanism in the inter-electrodes gap at low voltages; at higher biases ( $>350$  V), a significant current increase was observed and was ascribed, according to the SCLC model, to the filling of traps in the inter-electrodes gap. Such model enabled us to estimate the position of the dominant trap level at 0.56 eV below the conduction band. This value is compatible with the position of the excited state of the negatively-charged NV center.

In the low-current-injection regime a linear increase in the  $NV^-$  charge state population at the expense of the neutral charge state  $NV^0$  was observed by ensemble PL spectral measurements at increasing injected currents. Consistently with the above-mentioned SCLC model, this process was interpreted as the result of trapping of electrons injected in the active region of the device. The electrical control of the NV charge state enabled to reach a  $\sim 75\%$  fraction of negatively charged NV centers upon the injection of a stationary 400 nA current. While these results indicate a clear trend

in the stabilization of the negative charge state at the ensemble level, it cannot be ruled out that such effect is a dynamic result of recurring trapping/detrapping events at individual sites. A clarification on this point will require a thorough investigation at the single-photon emitter level with a confocal setup, involving the fast detection and monitoring of the PL emission of individual NV centers [18]. The high current-injection regime was associated with an intense EL emission. Differently from devices fabricated by He<sup>+</sup> ion irradiation [29], the implantation of C<sup>3+</sup> ions prevented the formation of additional color centers related to foreign impurities in the diamond lattice. Interestingly, previously unreported sharp EL emission peaks at 563.5 nm and 580 nm were observed, exhibiting a stronger dependence from the injected current with respect to the NV<sup>0</sup> center. These emissions were tentatively attributed to interstitial defects, consistently with previous CL studies [44,47]. Finally, the PL contribution of NV<sup>-</sup> centers in high current-injection regime indicated a decrease in the negatively-charged concentration of the NV defect, consistently with an increased hole current injection in the device or, alternatively, with a high-rate thermally-stimulated electron detrapping process associated with the Poole-Frenkel conduction mechanism.

Apart from shedding light on the fundamental mechanisms underlying charge state modifications of NV centers in diamond, the results reported in this work prospect promising applications in the development of solid-state devices for quantum technologies applications, where the independent control of individual defects with a large spatial density will be mandatory. These applications will require an improvement in the spatial resolution of the electrodes and a concurrent decrease in the inter-electrode distance. These goals can realistically be achieved by exploiting of already demonstrated advanced ion-beam-lithography techniques based on implantation masks with sub-micrometric spatial resolution [27], and should be combined with deterministic implantation and detection techniques [49-51] for the formation of individual defects at pre-selected positions of the device. This would offer the significant advantage of achieving high state conversion efficiency in bulk diamond while significantly reducing the operating voltage and still enabling the spin control of the defects with the utilization of standard surface electrodes. In perspective, these developments

could contribute to stabilize the charge state of deep NV centers preventing an uncontrolled blinking. The technique can thus enable the preparation and control of the charge state of deep NV centers (which are known to be characterized by better spin coherence properties with respect to superficial defects), thus leading to promising applications in quantum computing and quantum sensing.

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