Nitrogen-vacancy centers in nano-diamond reversibly decrease the luminescence quantum yield under strong pulsed-laser irradiation

Taras Plakhotnik and Robert Chapman
School of Mathematics and Physics, The University of Queensland, St Lucia, QLD 4072, Australia
E-mail: taras@physics.uq.edu.au

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Abstract. An unusual two- to threefold decrease in the luminescence intensity of nitrogen-vacancy centers in 30 nm diamonds under increasing pulsed-laser irradiation (up to the level of 0.1 J cm$^{-2}$) has been measured. The effect showed little dependence on the pulse repetition rate below 1 MHz and was accompanied by insignificant changes in the emission spectrum. The primary cause of the effect was attributed to the heat generated by the laser pulse and the consequent increase of the crystal temperature, which was estimated in the range of 300–400 °C.

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1 Author to whom any correspondence should be addressed.
1. Introduction

Nitrogen-vacancy (NV) centers in diamond have recently attracted much interest in many areas of research due to their unique properties, such as magnetosensitivity [1], photo stability [2] and chemical inertia [3]. This makes the diamond-based material a promising candidate for various applications in nanotechnology [4]–[11]. The ongoing research also includes efforts directed towards further miniaturization of the luminescent diamonds [12, 13], aiming at 5 nm size and below. These few-nanometer diamonds will facilitate many applications, such as single nuclear-spin magnetometry [7]. In a recent paper [14], we proposed to use nano-diamonds as tiny temperature sensors, and related the first demonstration of such an application for this extraordinary material. In this paper, we report a novel phenomenon observed in 30 nm diamond under strong picosecond laser irradiation and analyse the possible origin of the effect.

2. Experimental

The experiments were carried out on diamonds with diameters distributed in the region of 20–40 nm. They were spread on a spinning fused quartz substrate and mounted on an XYZ stage in the focal plane of a microscope objective. These diamonds were then excited with 532 nm light generated by a pulsed fiber laser (Fianium). The laser-pulse length was about 80 ps and the repetition rate was variable in the range from 1 MHz down to 10 KHz. The laser emission was focused on the substrate in a spot of about 25 µm in diameter. The highest excitation energy density at the location of the nano-diamond (determined for a single-laser pulse) was estimated at the level of \( E = 0.1 \text{ J cm}^{-2} \). The photoluminescence signal was collected using 0.9 NA (Olympus) and 0.7 NA (Nikon) infinity-corrected microscope objectives. The background emission was filtered out using a long-pass filter (transparent at wavelengths longer than 560 nm) and a band-pass filter (passing the wavelength range of 675–700 nm). The filtered light was then focused on the photosensitive area of an electron multiplying CCD (EMCCD, Andor). We also had a spectrometer installed so that the luminescence spectra could be measured for a selected diamond crystal. The spectrometer slit was opened wide during the measurements so that spectra of several diamonds could be obtained simultaneously. The diamonds were of the high-pressure high-temperature (HPHT)-type and were ordered from Academia Sinica, Taiwan. The NV centers were produced using the conventional procedure that involves irradiation with high-energy particles followed by 3 h annealing at about 750 °C.

3. Results and discussion

The 532 nm laser radiation excites the NV centers from their ground triplet state to the phonon band of their first electronically excited triplet state. This excitation is followed by fast phonon-assisted relaxation to the bottom of the excited state and by broadband luminescence centered around 680 nm. First, we measured the dependence of the luminescence intensity on the energy of the laser pulse. The results are shown in figure 1 as a log–log plot. Note that the luminescence intensity first increases linearly with the pulse energy, and then the curve bends down and starts to approach monotonically a maximum value. But at some point on the energy scale the luminescence signal suddenly begins to descend as the excitation energy further increases. This is quite a remarkable result because the saturation law for short-pulse excitation with a relatively low repetition rate is very simple and depends on very few parameters. The 80 ps pulse length
Figure 1. Saturation of luminescence in a nano-diamond excited with 80 ps laser pulse. The dots represent experimental points measured with the microscope objective NA 0.7 at 1 MHz pulse repetition rate and the squares are obtained with 100 kHz pulse repetition rate. The solid line is a chi-squared fit of the first nine points (up to the energy of about 0.1 µJ). There is good agreement between the experimental points and the theoretical curve for the lower-energy part of the curve but then the intensity of the luminescence drops by more than a factor of two for both repetition rates. Note that the average power of the laser was 10 times smaller at the lower repetition rate. The inset shows the change of luminescence intensity measured with the microscope objective NA 0.9 in another crystal for which the spectra were also taken (see figure 2) and where the intensity reduction is by a factor of three.

used in this experiment is much shorter than the relaxation times between the electronic states in the NV center. The fastest relevant relaxation rate in an NV center is the relaxation between the excited triplet electronic states and the ground electronic state [15]. This relaxation rate is on the order of 100 MHz, which is two orders of magnitude slower than the laser pulse length scale. In such a case, the rate of change in the population of the ground state reads as a product of $\sigma$, the absorption cross-section; $I$, the intensity of the laser irradiation at the location of the crystal; and $n_1$, the population of the ground state. All other transitions between the states in the NV center do not contribute to the dynamics because they are much too slow. Thus, $d n_1 / dt = -\sigma I(t) n_1$.
holds for the ground state population dynamics during the laser pulse with high accuracy. The solution of this equation is simply

\[
n_1(t) = n_1(0) \exp \left( - \int_0^t \sigma I(\tau) \, d\tau \right).
\]  

(1)

If in addition the longest relaxation time in the system is much shorter than the time between the consecutive laser pulses, then the population at the beginning of the laser pulse does not depend on the pulse energy because the relaxation to the ground electronic state will be completed before the next pulse arrives. In such a case, the luminescence signal \( R \) simply will be proportional to the depletion of the ground state and thus

\[
R = R_\infty \left( 1 - \exp \left( - \int_0^t \sigma I(\tau) \, d\tau \right) \right) = R_\infty \left( 1 - \exp(-\sigma \Phi) \right),
\]  

(2)

where \( \Phi \) is the energy flux through a unit area generated by a single pulse at the location of the NV center and divided by the energy of a photon with 532 nm wavelength. The slowest electronic energy relaxation rate in the NV center is around 3 MHz \([15]\) (compared to the 1 MHz repetition rate of the laser pulses). This is the rate from the singlet state to the \( z \)-spin state of the ground triplet state. The significance of this transition is further reduced by optical spin polarization, which eliminates the population of the \( x \)- and \( y \)-sublevels of the spin (see \([15]\) and discussion therein) and therefore one can expect that the above condition is fulfilled. In addition to this argument, we have verified that the saturation curve does not change if the laser-pulse repetition rate is reduced to 0.1 MHz (this gives 10 times more time for the system to relax to the electronic ground state). The squares in figure 1 represent the low repetition rate data. Thus, we expect equation (2) to be very accurate and therefore the change in the scaling factor \( R_\infty \) must be the cause of the observed effect.

The scaling factor \( R_\infty \) depends on the number of NV centers in the crystal, on the luminescence quantum yield of the NV centers, and on the photon detection efficiency of the experimental setup. The photon detection efficiency does not depend on the laser-pulse energy and its absolute values will be of a little importance for this paper.

The number of NV centers may change because of photo bleaching. Although NV centers are known for their high photo stability, measuring the saturation curve shown in figure 1 twice, swiping the energy first up and then down, eliminated the possible contribution of degradation to the decrease in the luminescence intensity. The data points measured on the way up and on the way down deviate from each other significantly less than the size of the dip in the saturation curve. Therefore, we conclude that permanent photobleaching does not contribute significantly to the observed effect. However, a peculiar possibility of ‘dynamic bleaching’ exists in NV centers. NV centers can be transformed from a negatively charged NV\(^{-}\) form to ionized NV\(^{0}\) \([15]\)–\([17]\). The two forms of NV centers can be distinguished spectroscopically. The neutral form has its emission band centered at about 610 nm with a zero-phonon line located at 575 nm \([18]\). The negatively charged center has a zero-phonon line at 637 nm and a phonon band centered at 680 nm. To verify the absence of the spectral shift, the spectra of a single center were measured at low and high energies of the excitation pulse. For the crystal used in the measurement, there was a factor of two reduction in the luminescence intensity at the high level of the laser energy. However, the two spectra are practically identical (see figure 2). Note that the transmission band of the optical filter used during the measurements of the saturation curve was between 675 and 700 nm. The difference between the two spectra in this band was
Figure 2. Luminescence spectra measured in weak (dots) and strong (solid line) excitation regimes. No difference is observed. Both spectra are typical luminescence spectra of NV$^-$ centers in diamond. The spectra are normalized by the intensity integrated between 570 and 830 nm. The strong feature at the left edge visible under strong excitation conditions is the laser emission.

less than 10%. Therefore, conversion from NV$^-$ to NV$^0$ can be ruled out as a significant cause of the decreased emission at high-excitation energies.

Thus, the only plausible reason for the observed effect is a change in the luminescence quantum yield. Such a change was observed recently in experiments where emission of NV centers was investigated at elevated temperatures [14]. When the sample of nano-diamonds was heated up in an oven, the luminescence decreased quite sharply as the temperature increased. For example, ramping the temperature up from room temperature to 300 °C was reduced the emission by a factor of two. The decrease in intensity attributed to an increase in the nonradiative decay rate from the electronically excited state of the NV centers [14]. This attribution was supported by the increase in the saturation intensity in the continuous-excitation mode and the directly measured increase of the luminescence decay rate [14]. Thus, a temperature increase of up to 300 °C can explain the results of our experiments reported here. Since the diamonds were placed on a highly transparent substrate, the most probable mechanism of heating the diamonds was direct absorption by the diamonds themselves.

We can estimate the energy required to heat a 30 nm diamond crystal to 300 °C. It is instructive to express this estimate in terms of the energy of the 532 nm photons used for optical pumping. The specific heat capacity of a diamond is 0.63 kJ kg$^{-1}$ K$^{-1}$ and its density is $3.5 \times 10^3$ kg m$^{-3}$. Using these numbers one can calculate that a 30 nm crystal needs energy...
of about 25 000 nm photons to achieve a 300 °C rise in temperature. This puts some limits on the possible mechanisms of the heating. For example, direct excitation of the NV centers to the excited triplet electronic state, during which process about 25% of the absorbed energy is lost to the phonons of the crystal (that is to heat), is too slow to provide the required energy to the crystal. A more effective mechanism could be based on the NV center promotion to a higher electronically excited state followed by fast (on a sub-ps time scale) nonradiative relaxation back to the first excited state. However, absorption of $2.5 \times 10^4$ photons within 80 ps requires a several-femtosecond relaxation time, which is unrealistically short.

It is known from recently published results that the temperature of detonation diamond can be increased up to 900 °C by quite moderate (1 kW cm$^{-2}$) levels of laser irradiation [19]. The heating of the detonation diamond is facilitated by its amorphous and graphite-type region near the surface, which takes up more than half of the volume of the tiny 5 nm crystal. The HPHT diamond used in this work is significantly larger in size and less affected by surface imperfections. However, it is far from being an ideal diamond crystal. The presence of the shell in HPHT-diamond is identified by the characteristic 1600 cm$^{-1}$ G-band in Raman spectra [13]. Significant shortening of the luminescence lifetime, presumably caused by the graphite shell, was also observed. This lifetime increased when the graphite shell was partially removed (indicated by a decreased intensity of the G-band) [13].

The required absorption cross-section is of the order of $\sigma_a = 2.5 \times 10^4 \frac{hc}{\lambda E} \approx 10^{-13}$ cm$^2$, where $c$ is the speed of light, $h$ is the Planck’s constant and $\lambda$ is the excitation wavelength (532 nm). A question arises about quenching of NV luminescence by such a highly absorbent entity in the diamond nanocrystals. An estimate of the Förster transfer radius [20] between an NVcenter and an absorber with $\sigma_a \approx 10^{-13}$ cm$^2$ is of the order of 10 nm and thus the coexistence of a highly luminescent NV center and a highly absorbent nanostructure in a 30 nm crystal is a possibility. These arguments support the mechanism of heating through surface imperfection and graphitized shells, although more research is required to identify the exact pathways of the heat transfer and how the absorbed energy affects the luminescence of NV centers. A possible direct mechanism of luminescence lifetime shortening is spin depolarization (presumably facilitated by the temperature increase) in the electronically excited state. The spin $x$- and $y$-sublevels are usually optically depopulated (the process is called spin polarization) but have strong nonradiative decay rates to the single state [15]. Once the population of these two levels is restored, the overall luminescence yield will diminish due to the nonradiative transitions.

4. Conclusions

We have demonstrated that a short 80 ps laser pulse can significantly but reversibly affect the emission of negatively charged NV centers embedded in high-temparature high-pressure diamond. We have also shown that the effect depends on the energy of the laser pulses, but does not depend significantly on the pulse repetition rate below 1 MHz. The observed up-to-threefold decrease in the photo luminescence intensity in response to increased laser pulse energy is related to decrease of the luminescence lifetime and quantum yield, but not to the changes in the emission spectrum. Heat generated with laser light in approximately 30 nm nanocrystals used in the experiment has been suggested as a mechanism of the effect. The estimated temperature rise is in the range between 300 and 400 °C. The independence of the effect from the pulse repetition rate confirms a short timescale for the heating process. Further research should clarify
the mechanism and the physical process involved in shortening the luminescence lifetime. An open question is, for example, the validity of thermodynamic equilibrium conditions between different degrees of freedom in the crystal on the timescale of the laser-pulse duration. Spin depolarisation (equivalent to a rising spin temperature) has been discussed as a microscopic mechanism for the dropping quantum yield. Such a mechanism, if confirmed, may have wider implications for nanomagnetometry and quantum computing. In particular, our experimental results indicate the possibility of fast optically induced spin depolarisation as a counterpart of the already-known optically induced spin polarisation.

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