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Laser Induced Phase Transformations and Fluorescence Measurements from Nanodiamond Particles

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**LASER INDUCED PHASE TRANSFORMATIONS AND
FLUORESCENCE MEASUREMENTS FROM NANODIAMOND
PARTICLES**

By
Nicholas Videtich

A THESIS
Submitted in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE
In Physics

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0.2 Abstract

Nanodiamonds (ND) are an exciting topic of photonics research because of their controllable quantum optical behaviors. As a byproduct of their small size, they possess a relatively high surface to volume ratio, which in turn relates to their potential usefulness as carriers in biological applications. By using laser induced phase transformations to ultimately shrink the particles, a path toward bio-compatible quantum emitters is explored. Measured Raman scattering spectra clearly indicate that the reversible phase change of NDs occurs upon femto-second laser irradiations. ND with nitrogen vacancies can also be used as a stable room temperature quantum emitter. By coupling this fluorescent ND to plasmonic nanostructures, photoluminescence enhancement is demonstrated, increasing its viability for use. Furthermore, I will present the experimental technique, which measures the second-order correlation function that represents the output photon statistics

Chapter 1

Laser Induced Phase Transitions in Nanodiamond

1.1 Background

1.1.1 Phases of Carbon

Carbon is an allotropic material, which means that there are multiple different ways that carbon can bond together. The most well known of these are graphite, diamond, and amorphous carbon. Each of these three can have drastically different properties, as a result of their different structures. They also have different Raman scattering characteristics. Graphite has a hexagonal lattice, which is both soft and opaque, while diamond is transparent and also one of the hardest known materials.

Hybrid phases can also exist, with both diamond and carbon allotropes present. One particularly interesting phase is known as a carbon-onion, which consists of a diamond core, surrounded by several shells alternating between diamond and amorphous carbon. It has been demonstrated that via laser irradiation, there exists a reversible process from going between ND with an impure outer shell, to carbon onions, and then back to ND [20]. This is theorized to be a result of the laser being absorbed initially by the outer amorphous carbon layer, which heats the diamond, which results in a morphological change in the crystalline lattices of the diamond and amorphous carbon. This then results in a carbon-onion, which continues to absorb laser light, heating the particle, and eventually converting back to a transparent ND, as illustrated below:

1.1.2 Nanodiamond Powders

Nanodiamond powder is a material that has been gaining interest in multiple fields of research for its characteristics and relative ease of production. This powder typically consists of diamond particles on the order of 5 nm in diameter, to 100 nm in diameter, and can be produced either via chemical vapor deposition, or detonation synthesis. Much of the attractiveness of this material comes from its bio-compatibility [14]. Another important characteristic of ND is that it is far more reactive than bulk diamond, as a consequence of its relatively large surface to volume ratio. It has been shown that for particles of less

Figure 1.1: The ND initially starts with some impurities on the outer shell, which contribute to a higher absorption of the laser. This outer layer then heats up, converting more of the ND to amorphous or graphitic carbon, while maintaining a diamond core. The particles are then baked in a tube furnace, to eliminate the outer impurities and leaving the central diamond core.

than 5 nm diameter, roughly 20% of the atoms are on the surface. Given that many of the atoms on the surface are not fully bonded in with the rest of the diamond lattice, it is likely that impurities form on the surface, such as amorphous or graphitic carbon. A method to purify these particles is using a furnace to oxidize off the outer unwanted layers [14].

1.1.3 Raman Spectroscopy

Raman spectroscopy is a technique used to observe the unique vibrational, rotational, or other non-optical modes in a system. This is particularly useful in identifying particular materials based off of their unique emission shift. As opposed to Rayleigh scattering, which relies upon elastic photon scattering, Raman is a purely non-elastic process. This occurs when a photon of given energy scatters off of a material, and either donates or receives energy from the material. The interaction results in a shift in photon energy, either red-shifting or blue-shifting the photon, depending on if it donates or absorbs energy from the material. In order for a material to demonstrate this effect, it requires that its electric dipole polarizability must change with respect to the vibrational coordinate. The intensity of the scattering is proportional to the magnitude of this change. Raman shift is typically reported in wavenumbers, which has units of inverse length. This is given by:

$$\Delta w = \frac{1}{\lambda_0} - \frac{1}{\lambda_n} \quad (1.1)$$

where w is the Raman shift in wavenumber, λ_0 is the excitation wavelength, and λ_n is the shifted wavelength. For diamond, the characteristic Raman shift when excited by a 325 nm UV laser is 1328 cm^{-1} , and is referred to as the D-band [14]. This corresponds to a peak only present within the diamond lattice. For a 'black carbon,' or graphitic carbon without the presence of diamond, this peak disappears, and instead only the G-band peak

is seen, at $\sim 1600\text{ cm}^{-1}$. This can be used as a measure of proof for whether or not a diamond lattice is present.

1.2 Experimental Outline

Solutions of varying concentration of ND particles in absolute alcohol are drop casted onto several different substrates, including glass, sapphire, silicon, and 100 nm SiO_2 on silicon and allowed to evaporate. These are then passed under a focused Titanium Sapphire laser system operating at 1.1 Watts, and a central wavelength of 800 nm. The beam spot is on the order of a few micron. The conversion from ND to is very visible, and then Raman spectroscopy measurements are conducted to verify the presence and conversion from a more pure ND state to an outer layer of amorphous carbon. The samples are then annealed in a tube furnace at $425\text{ }^\circ\text{C}$ for several hours in order to remove the amorphous and graphitic carbon, leaving behind the inner diamond core. These samples are then again measured with Raman spectroscopy to confirm that the amorphous carbon is removed, and to verify the presence of the crystalline diamond.

1.3 Results and Discussion

After laser irradiation in a grid pattern of varying intensity and duration, the diamond film appears as shown below in figure 1.2. This clearly shows that the amount of ND affected by the laser beam is intensity dependent, and that there is some threshold beam energy required in order for the conversion to occur. The shows increasing exposure time from right to left, and increasing beam power from top to bottom. The beam size was held constant at all points. Based off of the appearance alone, however, it is not possible to tell whether or not diamond is still present on the outer shells of the ND particles, so Raman spectroscopy must be used.

Figure 1.2: ND powder on sapphire substrate after irradiation of varying intensity and duration.

The spectra for Raman results at two separate points on the grid are shown below, in figure 1.3a and 1.3b. These also support the theory that there is indeed a minimum threshold beam intensity required to produce the phase change that is sought.

(a) Raman spectra for ND on sapphire (b) Raman Spectra for ND on sapphire after treatment with incident power of 0.3W. after treatment with incident power of 0.9W.

Figure 1.3: The Raman spectra across the two separate rows of the grid indicate that below some threshold power, the diamond peak is always present. After increasing the power, there exists some point where the incident power is high enough to cause the change, after some minimum exposure time.

These results agree with those reported by [14], however, are different in that Osswald's samples were suspended in liquid, whereas these samples were deposited on substrates. Based off of these results, another sample was prepared with a much larger area of the diamond treated by the laser, and then baked in a tube furnace in an attempt to remove the outer impurities of the ND particle, and leave behind a smaller pure ND particle. Raman measurements were conducted on the sample in its initial condition, after laser treatment, and then again after thermal treatment. These are shown below in figures 1.4a-c.

Figure 1.4: These three points of Raman data indicate that the ND particles are going through an intermediate phase with amorphous carbon present, and then after thermal treatment return to a more pure diamond state.

1.4 Conclusions and Future Work

These results indicate that it is possible to induce phase transformations in ND particles via laser irradiation. This irradiation assists in the conversion of the outer layers of ND from mostly diamond lattice to amorphous carbon. Then, with the use of a tube furnace, the outer amorphous diamond may then be baked off, leaving a diamond core. Based off of this procedure, ND particles of a given size may be reduced to a smaller size, potentially to a quantum emission regime. In order to verify size reduction, the particles need to be measured under TEM initially, and then measured again after processing. In order to verify quantum dot behavior, the samples should exhibit discretized emission when optically pumped, based off of their size.

Chapter 2

Fluorescence Measurements from Nanodiamond with Nitrogen-Vacancies

2.1 Background

2.1.1 Optical Trapping

Laser based optical trapping is a technique that has been used since the early 1970's, when it was first demonstrated by Arthur Ashkin, to levitate micron-sized dielectric particles in both air and water [13]. This technique has since been used to trap single neutral atoms, as well as bacteria and viruses. The trap itself works by focusing a laser beam through a high numerical aperture (NA) objective lens, which then will result in a dielectric particle near the focus to experience a force from the momentum transfer of scattered photons. Recent work has demonstrated that this can be done with a low numerical aperture lens, and the addition of a spatial light modulator [3], or by splitting the initial trap laser into two beams, and focusing on the target from above and below [19], however, neither of these methods will be discussed further.

The force that the particle experiences from the trap laser acts both in the direction the light is propagating, as well as a gradient force in the direction of the spatial light gradient. The first is the more simple to understand, as the beam is pushing the particle in its direction of travel. The second, however, is what allows the trapping to actually occur. By using a high NA lens, the beam has a steep intensity gradient, which in turn causes the particle to experience a confinement force. This results from the inhomogeneous electric field of the laser inducing fluctuating dipoles within the particle, which then experience a force in the direction of the field gradient.

For particles much larger than the wavelength of the trap laser ($\alpha \gg \lambda$), the particle satisfies the conditions of Mie scattering, so the forces may be calculated based off of ray optics. When the light refracts within the sphere, the momentum of the photons change, and as such the sphere experiences a momentum change equal and opposite that of the photons. This force is therefore related to the intensity of light incident. Depending on

the direction of refraction, the sphere will experience a force either in the direction, or opposite the direction of the intensity gradient.

For particles much smaller than the wavelength of the trap laser ($\alpha \ll \lambda$), the particle satisfies the conditions for Raleigh scattering, and the forces may be calculated by treating the particle as a point dipole. Again, the direction of the force experienced is based off of the ratios of the indices of refraction between the particle, and the medium it is in. In addition, the polarizability of the sphere must also be taken into account to accurately calculate the force.

The third case, for which the particle is on the same order of size as the wavelength of the trap laser ($\alpha \approx \lambda$), however, a hybrid approach between the two must be taken. A more complete discussion of the theory behind this case can be found in [21].

It has been demonstrated that the effectiveness of the optical trap can be enhanced in the presence of a nanostructured substrate. By using pairs of gold nanodots and a standard optical trapping setup, subwavelength atomic traps have been demonstrated that increase the trapping efficiency and reduce the trapping volume beyond the diffraction limit [7].

2.1.2 Fluorescent Nanodiamond

Fluorescent nanodiamond general refers to nanometer scaled particles of diamond with crystalline defects of vacant carbon atoms, replaced by nitrogen. Nitrogen is already the most common impurity in diamond [17], however, in order to create a higher concentration, additional processes can be used. One such process involves bombarding nanodiamond particles with ionized atoms, where the collisions force out carbon atoms, and creating vacancies. By then thermally annealing at 800 °C, the moving vacancies in the particles are trapped by pre-existing nitrogen atoms, which forms a nitrogen vacancy center (NVC) [18]. Another possibility is that the nitrogen atoms instead form a nitrogen-vacancy-nitrogen complex (NVN), which has different fluorescent characteristics, as shown below in figure 2.1b [17].

Figure 2.1: The fluorescent spectra of nanodiamond with NVCs, (a) and NVNs (b), optically pumped by 532 nm and 443 nm light respectively[17]

Nanodiamond with NVCs will be the focus of this discussion, as they will be used in the experiment. There are two separate types of NVC, each with different charge states, which correspond to different peaks in the spectrum of fluorescing nanodiamond. The peak at 575 nm corresponds to a neutral NVC, commonly denoted as NV⁰, and the other is a negatively charged NVC, denoted as NV⁻. These are the peaks at 575 nm, and 637 nm. The two separate peaks from the different NVCs are the zero phonon lines (ZPL) corresponding to each case, which occur when photons of appropriate energy are absorbed, and excite an electron without coupling with a phonon mode of the crystalline lattice. Those that do couple with a phonon mode of the lattice contribute to a much broader emission spectrum of light with longer wavelength. This process typically requires low temperatures on the order of 40 K to even see the ZPL emission, however, due to the strong coupling of NVCs with the diamond lattice, they are observable at room temperature in fluorescent ND.

In addition to stable photon emission at room temperature, the negatively charged NV⁻ center can be utilized as a quantum bit, by optically measuring its free electron spin [6].

2.1.3 Photon Statistics

The degree of coherence for light can be measured using a Hanbury Brown and Twiss (HBT) interferometer. In order to measure degree of coherence, a Hanbury Brown and

Twiss interferometer is used. This consists of a 50:50 beamsplitter, two Single-Photon Avalanche Diodes (SPADs), and a Time-Correlated Single Photon Counting (TCSPC) system. This system records detection events from the pair of SPADs, and compares the time window between each detection. This technique was pioneered in 1956, when two photomultiplier tubes were used to collect data from the Star Sirius, with the aid of some large mirrors. Despite no information about the phase of light being collected, the two detectors recorded an interference effect, further indicating a positive correlation between the two signals [8].

Light can be classified based off of the second order coherence function into three separate categories: Bunched, random, and antibunched. The normalized second order correlation function can be written as:

$$g^{(2)}(r_1, t_1; r_2, t_2) = \frac{\langle E^*(r_1, t_1) E^*(r_2, t_2) E(r_1, t_1) E(r_2, t_2) \rangle}{\langle |E(r_1, t_1)|^2 \rangle \langle |E(r_2, t_2)|^2 \rangle} \quad (2.1)$$

However, if working with light in the classical regime, this can be rewritten in terms of intensities:

$$g^{(2)}(\tau) = \frac{\langle I(t) I(t + \tau) \rangle}{\langle I(t) \rangle^2} \quad (2.2)$$

The function relates the probabilities of photon detection events from a detector at a specific time, with another detection event at some time delay, τ . It can be shown that the function is even, so:

$$g^{(2)}(\tau) = g^{(2)}(-\tau) \quad (2.3)$$

For the case of a coherent signal with constant intensity, it is easily seen that

$$I(t) = I(t + \tau) \quad (2.4)$$

So the correlation function simplifies to

$$g^{(2)}(\tau) = \frac{\langle I(t)^2 \rangle}{\langle I(t) \rangle^2} = 1 \quad (2.5)$$

In the case of bunched light, which consists of a stream of photons which are bunched together, it is expected that there will be a higher probability of detecting a second photon at some short time delay from the first. Therefore, the value of $g^{(2)}(\tau)$ For short delays should be greater than 1, and should decrease as the time difference increases. Therefore

$$g^{(2)}(0) > g^{(2)}(\pm\infty) \quad (2.6)$$

A special case of this occurs when the value of $g^{(2)}(0) > 2$, which is referred to as superbunching. This occurs when a group of emitters couples together, and oscillates as a single large dipole and emits photons at an enhanced rate. The theory behind this has been described previously by Dicke [4].

The third case is a purely quantum state, which requires single photon emission. In this case, there is a stream of single, spaced photons. As a result of this, when one detector is

triggered, it is impossible for the second detector to record an event within the time before the next photon arrives. This means that the function will show:

$$g^{(2)}(0) < g^{(2)}(\tau) \quad (2.7)$$

and

$$g^{(0)}(\tau) < 1 \quad (2.8)$$

In order to test which regime emitted light from a sample falls into, an HBT interferometer setup is required. This requires the use of a 50:50 beamsplitter to separate the incident signal, and send them onto two separate single photon counting modules (SPCM). These two detectors are then connected to a Time Correlated Single Photon Counting (TCSPC) system, which collects the pulses from the detectors and starts and stops an electronic timer and counter. This both counts the events and the time windows between each event, which will typically be presented in a histogram, showing the number of events for each particular time interval. Visually, for the ideal cases, this will appear as in the figure below:

Figure 2.2: A visual representation of the three separate regimes of light as recorded by a HBT interferometer. The widths of each the two curves for both bunched and antibunched light are not necessarily going to have this specific width. The actual widths depend on the coherence lengths of each of the specific sources.

A special case occurs when the value of $g^{(2)}(0)$ is greater than two. This refers to a phenomena known as superbunching, which indicates an enhancement in the emitted photons from the sample.

A potential issue that may arise, giving what appear to be non-physical results is known as the afterglow effect. This occurs when a photon is absorbed by a detector, and then the detector emits spectrally broad light as the electron avalanche occurs [5]. This emission can then be detected by the second detector, or indeed a reflection can be detected by the same detector, which causes large correlated peaks within the recorded data. In order to avoid this, two identical interference bandpass filters should be used on the detectors to avoid these additional photons from being detected.

2.1.4 Purcell Factor

For a two level system coupled to a single-mode resonant cavity, the emission is different than that of an isolated system. This is known as the Purcell effect. The Purcell factor itself, which is given by:

$$F_p = \frac{3Q\lambda^3}{4\pi^2 V_0 n^3} \xi^2 \frac{\Delta\omega_c^2}{4(\omega_0 - \omega_c)^2 + \Delta\omega_c^2} \quad (2.9)$$

where Q is the quality factor of the cavity, λ is the free space wavelength of light, n is the refractive index of the medium, ω_0 is the natural frequency of the transitions, ω_c is the frequency of the cavity mode, V_0 is the volume of the cavity, and ξ is the normalized dipole orientation factor given by:

$$\xi = \frac{|p \cdot \epsilon|}{|p||\epsilon|} \quad (2.10)$$

The Purcell factor describes whether or not a cavity enhances or inhibits the rate of spontaneous emission, which correspond to values greater or less than one.

2.2 Experimental Outline

Given that NVCs are already demonstrated to exhibit superbunching in room temperature [2], it may be possible to further enhance this by coupling the diamond to a plasmonic structure. By optically trapping single diamond nanoparticles near plasmonic structures, measuring the photoluminescence (PL) spectrum of the particles to verify the presence of the nanoparticles, and then conducting measurements of $g^{(2)}$, this is explored.

2.2.1 Optical Setup

A custom microscope setup is used for the experiments, as shown below in figure 2.3.

Figure 2.3: The custom built microscope setup. A custom built 1064nm Nd:YVO₄ trapping laser is coupled to a fiber, and sent from below through a 100x high NA oil immersion objective, while the 532 nm excitation laser is directed downward by a 50:50 beamsplitter onto the sample. The signal is then collected by the same objective, and passed through a 90T:10R filter, where the reflected signal is sent to a CCD camera for imaging. The signal that passes through is sent through a longpass 567 nm filter, and a shortpass 750 nm filter to remove any residual excitation and trapping laser. The light is collected by a lens, and sent via fiber to either a spectrometer or HBT setup for measurement. A white light scattering arm may also be used to better image the samples.

The custom microscope uses an oil immersion lens, such that the ND may be placed directly in the oil to avoid any issues with index mismatching that would be introduced by the use of a cover slide [19], as well as to prevent the particles from being outside the working distance of the lens. The trap laser used is a custom built Nd:YVO₄ laser, which may be used at anywhere between 80mW to greater than 5 Watts of optical power. This laser also features a custom made water cooling system, to ensure long term beam stability.

In order to measure the second order correlation function, an HBT setup was constructed, as shown above. This makes use of two single photon avalanche photodiodes, as well as a 50:50 beam splitter, and a picosecond precision TCSPC system.

For the cases when the second order correlation function is measured, the light is first passed through a monochromator set to 637 nm before going to the HBT setup, to ensure that only emission from the NV⁻ ZPL line is measured.

2.2.2 Sample Preparation and Measurement

First, a clean piece of silicon is used as a test piece to verify the functionality of the HBT setup. This sample is only irradiated with the 635 nm excitation laser, and then the light is passed through a monochromator set to 635 nm, to ensure no stray light enters the setup. This measurement should yield a $g^{(2)}$ value of 1, indicating only coherent laser light is being measured.

Fluorescent nanodiamond in DI water (Sigma Aldrich, average diameter 90 nm, >500 NVC/particle) is originally placed on a substrate containing a plasmonic nanostructure consisting of either a metal-insulator-metal (MIM), or metal-insulator (MI) stack, and the water allowed to evaporate. These structures were fabricated at NIST, and are shown below in figures 2.4a and 2.4b.

(a) The MI structure

(b) The MIM structure

Figure 2.4: SEM images showing the MI and MIM structures

This leaves a layer of ND on the sample, covering both the structures and plain substrate. These samples provide comparison data for large numbers of ND, for both PL and $g^{(2)}$ data, with measurements taken on and off of the structures.

NDs are also then mixed into immersion oil, at varying concentrations to optically confine single NDs both near the MI or MIM structures, and on plain glass for comparison.

Signal from the samples is sent via fiber to either a spectrometer for PL measurement, or via fiber to a monochromator, and then via fiber to the HBT setup. All HBT data was recorded using a PicoQuant HydraHarp TCSPC system, and the results calculated using PicoQuant QuCoa software.

2.3 Results and Discussion

The photoluminescence results for the ND in relatively large quantity on an MI structure are shown below in figures 4. The difference in signal strength is clearly seen between the data taken above a structure and off of the structure for the MI sample. This indicates that somehow the nanostructures are enhancing the signal, perhaps by the ND particles coupling to them.

(a) MI Structure large quantity ND

Figure 2.5: PL data for an MI structure with a large quantity of ND. The signal enhancement above the structure indicates that the MI structure is enhancing the emission rate of the ND.

(a) Laser signal

(b) ND on glass

The HBT data, shown above in figures 5a and b, appears to show that the system shows the correct result for a coherent source of light, and indicates standard bunching behavior for the ND as anticipated. These two pieces of data verify the functionality of the setup.

The results for measurements from the MI and MIM structures are shown below, as well as a measured dispersion graphs from each sample, showing the overlap in photon energy with the resonance of the structure.

Figure 2.7: Initial $g^{(2)}$ results. These results seem to indicate a reduction in bunching strength.

In both cases, it appears that the bunching is actually reduced as compared to the plain ND. This could be a result of the overlap between the ND emission energy and the resonance of the structures causing the emission to trend toward random emission. With a sufficiently higher power combined with a closer overlap in resonance and emission, this could potentially show lasing.

2.4 Conclusions and Future Work

The results presented indicate that fluorescent ND exhibits enhanced emission by coupling to MI structures. The results also indicate that two structures reduce the magnitude of bunching, and increase how random the emission is. In order to further investigate this, a pulsed excitation laser source will be used. The higher peak powers present from the pulsed source make it more likely to see higher order effects, and also increase the likelihood of the samples behaving as lasers.

At present, work is also being conducted in order to experimentally verify the presence of optical trapping. This can be done a variety of ways, such as using a quadrant photodiode (QPD), which maps the location of incident light on four separate quadrants of a photodiode. This outputs a signal which allows the position of a particle to be mapped.

A second option for verification of trapping involves using a much larger dielectric particle ($\approx 2\mu m$), which allows the particle to be observed visually within the trap. The particle should exhibit Brownian motion within the trap [7].

A third option for verification of trapping utilizes the PL emission of the ND particles. By increasingly lowering concentrations of ND in immersion oil, there should exist a threshold where upon turning off the trap laser, so few particles should remain in the confocal volume of the excitation laser that no significant PL is measured. Then, if the trap laser is turned back on, the signal should return, as particles are once again trapped in the excitation beam.

After optical trapping is verified, single particles of ND may then be trapped near the plasmonic structures, and the PL spectrum and $g^{(2)}$ may then be measured. These results should definitively prove whether or not plasmonic nanostructures can enhance the super-bunched emission of single ND particles with NVCs. Further work may then be conducted, pending the results for higher NVC concentrations, with ND that has far fewer NVCs, to see if there is a dependence upon the quantity of NVCs within each particle. The particles may also be tested near other plasmonic structures with different periodicities, in order to investigate the coupling efficiency of the ND.

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