

# Toward Engineering Fluorescent Nanodiamonds

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## ABSTRACT

We have grown nanodiamonds (NDs) with Silicon vacancy (SiV) and Nitrogen vacancy (NV) color centers starting from organic precursors in a diamond anvil cell (DAC) using both resistive and laser heating methods. High resolution transmission electron microscopy (HRTEM) measured a size range of 2 -100 nm, and photoluminescence (PL) and optically detected magnetic resonance (ODMR) analysis found evidence of the NV and SiV centers. Our results imply that it might be possible to grow fluorescent nanodiamond by a high-pressure high-temperature (HPHT) organic “seeding” process. Such a process is possible if the temperatures and pressures are low enough to allow the creation of diamond without decomposition of an initial organic seed molecule (such as Adamantane). The concept of using an organic seed to grow nanodiamond would have benefits such as pristine surface quality and the deterministic creation of color-centers at the center of the nanodiamond, giving rise to better fluorescence properties than current probabilistic methods. Such high-quality nanodiamonds would have major impacts in fields such as biology, metrology and quantum information sciences.

Keywords : Nanodiamonds, Nitrogen Vacancy Center, Molecular Imaging, Bio-Markers, High-Pressure High-Temperature

## INTRODUCTION

Nanodiamonds with fluorescent color centers have numerous applications like non-bleaching labeling of biomolecules, fluorescent markers for drug delivery [1], and nanoscale sensors of local environments [2]. For example nanodiamonds containing NVs have been proposed as sensors for a variety of magnetic species in cells, like radicals [3], protons or phosphorous nuclei [4], and also as sensors of local electric fields [5] and temperature [6]. However, in order for many of these applications to succeed ultra-small nanodiamonds (< 10nm) having at least one photostable fluorescent color center per crystal are needed. For biological applications small nanodiamond size is preferred so that they can easily fit into cellular compartments and/or membranes [7] and eventually be cleared by the kidneys of mammals [8]. However, until now the smallest nanodiamonds with stable fluorescent emitters are harvested from meteors; specifically ~1.6 nm with photostable silicon-vacancies (SiV) [9]. In the case of NV color centers, they are rare in nanocrystals under ~7 nm [10]. Although there have been isolated reports of NV's in crystals down to 5 nm they often exhibit PL “blinking” and do not usually show good ODMR contrast [11].

Current techniques to grow ultra-small nanodiamonds typically degrade the purity of the resulting nanocrystal hindering the most sensitive sensing capabilities. Furthermore, the creation of color-centers inside nanodiamonds is typically probabilistic

relying on techniques such as irradiation and annealing of the nanodiamond which tend to place the color-centers near the surface resulting in poor fluorescence and coherence properties due to phenomenon such as surface spin traps [12].

In this paper we report on the high-pressure high-temperature (HPHT) formation of stable color centers in nanodiamond using a diamond anvil cell (DAC) and laser or resistance heating. The starting material is an organic molecule, such as Adamantane, mixed with a secondary quantity to create the appropriate color center (such as Silicon Powder to produce SiV's). Our results imply that a seeding technique to engineer NDs with pre-determined color centers using HPHT might be possible, allowing pristine surface quality and optimum placement of a variety of color-centers. Furthermore, aside from the benefits to scientific applications such a technique would also be a simpler and industrial- scalable method as opposed to current CVD techniques [13].

## RESULTS

Figure 1 presents results from DAC laser heating experiments where photostable SiV and NV centers were created in NDs with sizes ranging between about 20-100 nm. The initial charge was Adamantane doped with a small amount of Si or the N containing organic compound AZADO. Growth temperatures for the laser heating experiments were typically measured to be between 1000 – 1700 °C, and the pressures were between 20-30 GPa. The resulting NDs with color-centers were created by the decomposition of the organic compounds inside the DAC due to the high temperatures induced by laser heating. Figure 1a gives a bright SiV PL spectrum with inset showing the magnification of the 1st order ND Raman peak (~ 571nm). The PL and ODMR spectra in Figure 1c and d, which are signatures of the NV center, were taken from a laser heated experiment using AZADO. The double resonance seen in the ODMR is typically due to excess strain inside the diamond lattice, implying that the synthesized NDs contained numerous defects. The *in situ* Raman spectra in Figure 1b are of the carbon-hydrogen (CH) stretch modes of Adamantane as the laser power (and hence the temperature) is

increased (direction of arrow). The degradation of the modes upon increasing temperature is due to the decomposition of Adamantane.

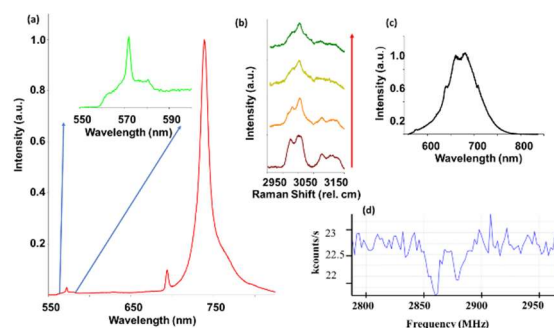


Figure 1 Data from DAC laser heating experiments on Adamantane and AZADO to produce fluorescent NDs. (a) PL spectrum of a synthesized ND with SiV's, the inset is a magnification of the first order ND Raman peak. (b) The CH Raman modes of Adamantane as the laser power is increased (direction of arrow). The degradation of the spectra is associated with decomposition of Adamantane, which is required to grow ND at the high temperatures induced by laser heating. (c) NV PL from a laser heating DAC experiment using AZADO. (d) NV ODMR signal from NDs produced from a laser heating experiment on AZADO.

To circumvent the problem of poor temperature control and large temperature gradients associated with laser heating, experiments were designed to heat the sample chamber using a resistance heater. Using this heating technique the decomposition temperature of Adamantane was measured to be around 600-700 °C for pressures around 20-30 GPa.

Figure 2 gives experimental data of ND growth from Adamantane at temperature and pressure conditions around the measured decomposition threshold using the resistance heating technique. Figure 2a depicts *in situ* Raman spectra of the CH stretching modes of Adamantane during the HPHT experiment. The shape and position of the CH Raman modes do not drastically change during the HPHT cycle implying that a substantial amount of the Adamantane did not decompose.

Figure 2b is an SEM image of sample extracted from another resistance heating experiment at similar pressure and temperature conditions as Figure 2a. Whereas it was difficult to measure the Raman spectrum of the sample, we were able to measure first-order nanodiamond Raman spectra ( $\sim 1328$  rel.  $\text{cm}^{-1}$ , (inset), with possible NV PL.

Note that the hole seen in the sample was “burned in” due to the 532 nm laser used to take the Raman spectrum recorded in the inset. This implies that the NDs are embedded inside of some type of organic matrix since ND will not decompose under the low power Raman laser.

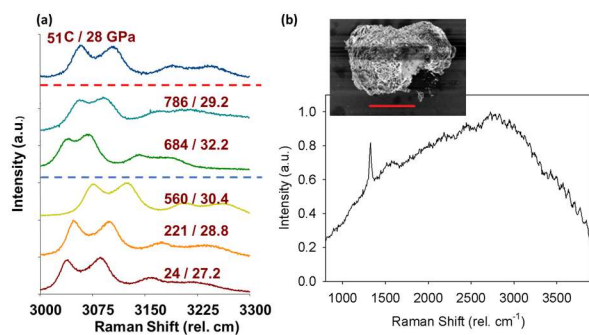


Figure 2 Experimental data proving the stability of an organic seed molecule at HPHT conditions that allow growth of nanodiamond. (a) In situ Raman spectra during a resistive heating experiment on Adamantane, pressures and temperatures are as indicated. The Raman spectrum after the high-temperature cycle (top curve) has a similar shape as the initial spectrum before the high-temperature cycle (bottom curve), implying that at the HPHT conditions Adamantane does not undergo substantial decomposition. The blue dashed line represents the region where a drastic shift in the Raman spectrum occurred. This shift may be due to a partial amount of the Adamantane. (b) ND Raman spectrum taken from a sample extracted from the DAC after HPHT (inset, the scale bar is 10  $\mu\text{m}$ ).

## CONCLUSIONS

The most interesting results from the resistance heating NDs is that the temperatures are substantially lower (about 300  $^{\circ}\text{C}$ ) than any other recorded HPHT synthesis from organic precursors

[14], which rely on the total decomposition of the initial organic charge. The difference in ND properties between the laser heating and resistance heating experiments show that the resistance heated product is most likely not due to total decomposition, which is also implied by the *in situ* Raman spectra during heating (compare Figure 1b and Figure 2a). It is therefore possible that the ND from the resistance heating methods are grown by seeding around an Adamantane molecule, which has a nearly exact match to the diamond lattice. For this to be successful some of the initial Adamantane must decompose into Carbon radicals, as indicated in the spectra of Figure 2a, which subsequently bond to a non-decomposed Adamantane molecule.

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