Effect of Annealing Temperature on Nitrogen Vacancy Formation in Nanocrystalline Diamond

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Summer Program(s): 2024 Global Quantum Leap International Research Training Experiences (GQL IRTE) Program at the National Institute for Materials Science (NIMS), Tsukuba, Ibaraki, Japan
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Primary Source(s) of Research Funding: NSF GQL IRTE Grant to University of Minnesota No. OISE-2020174
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Summer Program Website: https://cnf.cornell.edu/education/reu/2024

Abstract:

Nitrogen-vacancy (NV) centers are diamond lattice defects that are well-suited to quantum sensing. NV-rich nanodiamonds have wide sensing applications in biosensing and nanoelectronics. The present research investigates the effects of annealing temperature and oxygen treatment on NV formation and detection in nanodiamonds. Increasing annealing temperature combined with oxidizing the diamond surface was shown to improve nanodiamond composition and fluorescence.

Summary of Research:

NV centers are color centers in diamond that arise when a substitutional nitrogen atom pairs with a lattice vacancy. NV centers can be neutrally charged (NV^0) or negatively charged (NV^-). NV^- centers have received significant research focus in recent years due to their good quantum properties, such as a long coherence time, optical spin-state initialization, and optical spin-state readout. The spin-dependent energy levels of NV^- centers are sensitive to local magnetic fields, electric fields, temperature, and strain, making them very useful for quantum sensing applications. Nanodiamonds can be formed by crushing bulk diamonds, allowing for high spatial resolution quantum sensing experiments in biosensing and nanoelectronics [1].

Synthetic diamonds can be created by a high-pressure high-temperature compression of a carbon-rich precursor or via a chemical vapor deposition of a carbon-containing gas. Both methods introduce tunable levels of substitutional nitrogen into the diamond lattice [2]. The diamonds are then irradiated with a high-energy electron beam to create lattice vacancies. High-temperature annealing mobilizes the vacancies to pair with nitrogen atoms throughout the diamond lattice and form neutrally charged NV^0 centers. Negatively charged NV^- centers arise when a second substitutional nitrogen atom donates an electron to an NV0 center [3].

NV^- sensors exhibit maximal sensitivity when the NV^- concentration is maximized and the NV^0 concentration is minimized [2]. The current research examines what annealing temperature creates the most NV^- centers without creating a disproportionate amount of NV^0 centers in Tomei MD50 nanodiamonds after irradiating with a high-energy electron beam. The concentration of each NV center was measured by tracking their corresponding peak height on a photoluminescence (PL) spectrum. Measuring temperature-dependent changes in relative NV^0 and NV^- peak heights tracks the relative concentrations of the NV centers.

Due to non-constant sample volumes and graphitization, NV peak heights were determined relative to the phonon sideband such that the PL spectrum was normalized to the range [0,1]. Figure 1 shows the Tomei MD50 NV^0 and NV^- results. Increasing temperature leads to higher NV^-, but NV^0 increases faster and with a larger fractional change. Figure 2 shows that the larger fractional change leads to a declining ratio of NV^-/NV^T, where $NV^T = NV^0 + NV^-$. Higher temperatures also lead to increased graphite on the surface of the nanodiamonds, which significantly reduced the overall fluorescence of higher-temperature samples.

Graphitization on the surface of the diamond led to a blackening of the nanodiamonds visible to the naked eye. The effects of graphitization were counteracted by oxidizing at 550°C for three hours. Oxidizing the diamonds turned them white and increased their overall PL intensity by a factor of 10. Importantly, the two oxidized samples measured showed significant improvements in NV^- concentration and NV^-/NV^T, as shown in Figure 3 and Figure 4.

Conclusions and Future Work:

The present research supports the idea that, within the experimental temperature range of 900-1090°C, increased annealing temperature increases both NV^0 and NV^- concentration. However, higher temperatures seem to induce graphitization and a lowered NV^-/NV^T ratio. Oxidizing nanodiamonds rich in NV centers decreases graphitization, thus increasing the measured NV^- and NV^-/NV^T fluorescence. The inferential weight of these conclusions are limited by the non-constant sample volumes when using nanodiamond

samples. Furthermore, technical limitations prevented measuring the effect of oxidation at different samples on the same diamonds.

The present work focuses only on improving the NV composition of nanodiamonds. However, previous theoretical and experimental work on bulk diamonds suggests that improving diamond composition will improve the underlying quantum properties [2]. Future work is thus needed to measure the effects of NV^- and NV^-/NV^T concentration on T_1 relaxation time, T_2 relaxation time, and the T_2^* decoherence time.

Further research is also needed to determine the compositional effects of oxidizing nanodiamonds which were annealed at increasing temperatures.

Acknowledgements:

This work was made possible by Dr. Tokuyuki Teraji, Dr. Jun Chen, Dr. Takeyuki Tsuji, Dr. Yuta Masuyama, Mrs. Shoko Manako and Mrs. Miyuki Kameoka. Furthermore, this opportunity would not have been possible without the National Institute of Materials Science, the Global Quantum Leap International Training and Research Program, the Cornell NanoScale Facility, and National Science Foundation.

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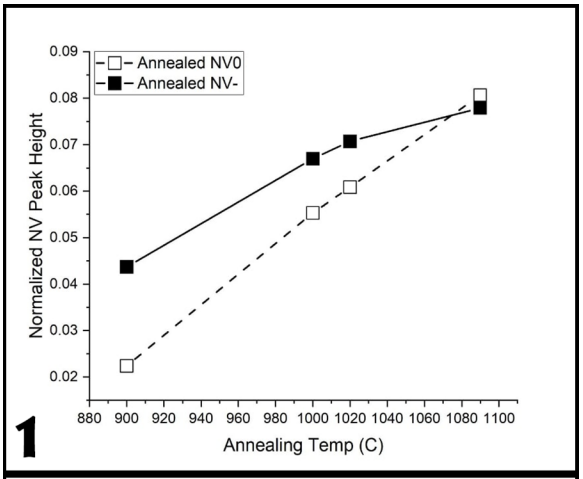

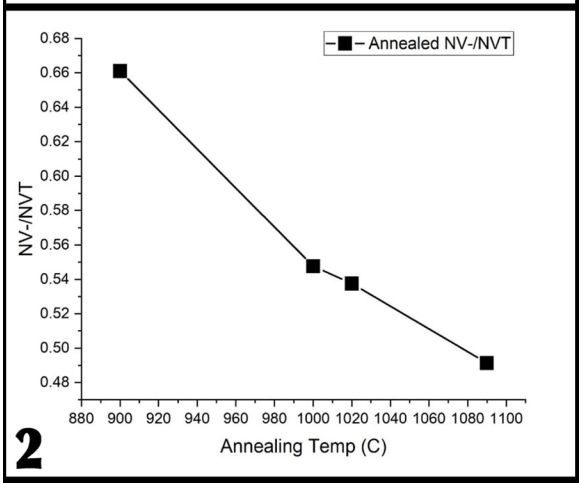

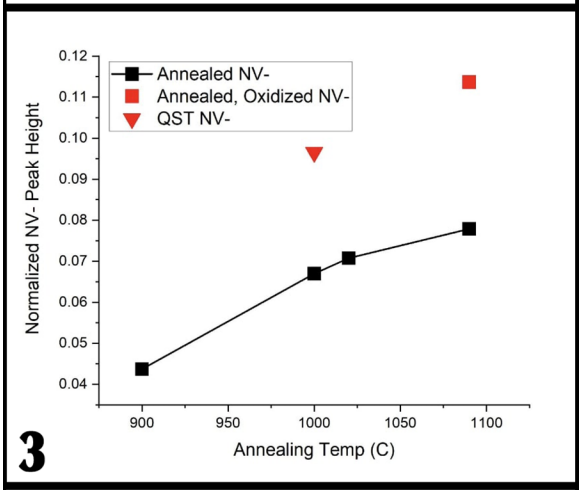

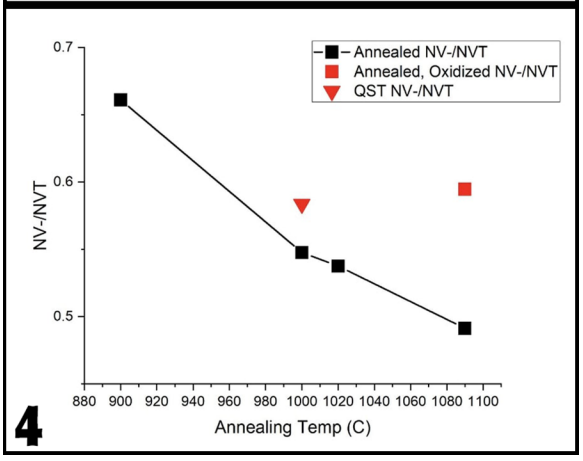

Figure 1: A plot of the NV peak height relative to the phonon sideband versus the annealing temperature. All samples were annealed under vacuum conditions for two hours. Both NV^0 and NV^- normalized peak heights increased within the experimental temperature range of 900-1090°C.

Figure 2: A plot of the NV^-/NV^T, where $NV^T = NV^0 + NV^-$. All samples were annealed under vacuum conditions for two hours. Both NV^0 and NV^- normalized peak heights increased within the experimental temperature range of 900-1090°C.

Figure 3: A plot of the normalized NV^- peak height for an annealing-only sample, an annealed and oxidized sample, and a second annealed, oxidized sample provided by the National Institutes of Quantum Science and Technology (QST).

Figure 4: A plot of the NV^-/NV^T ratio for an annealing-only sample, an annealed and oxidized sample, and a second annealed, oxidized sample provided by the QST.