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Low Temperature Studies of Nitrogen Vacancy Centers in Diamonds

J. CHENG, C. H. SHAM, K. W. CHENG and Tony K. C. HUI

Master Dynamic Ltd.

Dr. Stefan Bogdanovic and Prof. Marko Loncar

Harvard University

This research paper provides experimental data on the spectral characteristics of photoluminescence from the studied Chemical Vapor Deposition (CVD), Natural, and High Pressure High Temperature (HPHT) treated diamonds. The photoluminescence spectra of the several diamond defects has been measured in the temperature range from 4K to 300K. The temperature dependence of the Nitrogen Vacancy center Zero Phonon Line (ZPL) properties was demonstrated in several different diamond hosts.

Introduction

The nitrogen vacancy center (NV) in diamond, known to exist in negative (NV^-) and neutral (NV^0), has attracted intense scientific attention due to its outstanding electron spin and optical properties[1-6], which make it a promising system for a broad range of applications in the fields of quantum information processing[7, 8], high sensitivity magnetometry[9], and bio-medicine (e.g. fluorescent bio-markers)[10]. The identifying features of NV^- and NV^0 are their optical zero phonon lines (ZPLs) with wavelengths of 637nm and 575nm, respectively. The NV forms a ground state spin triplet that can be controlled coherently at room temperature using electric field, magnetic field, laser, or a combination of the above[11]. At cryogenic temperatures, the transitions between the triplet ground state and each of the excited states can be individually addressed via resonant optical excitation allowing single-shot readout of the electron spin state[12]. Furthermore, the spin-dependent optical transitions[13] provide an interface between spins and photons as needed in schemes for scalable quantum processing and long distance transfer of quantum information.

Low temperature performance of the NV centers is well documented in the recent literature. For example, Jelezko et al. revealed the linewidth of the individual NV defects in diamond nano-crystals at low temperature to be around 150MHz[14]. A. Drabenstedt et al. observed the linewidth of a single NV^- center in 100 μm thickness type Ib diamond is about 0.64 meV (0.21nm) at 4K[15]. V. Hizhnyakow et al. [16] investigated anomalous temperature dependence of the zero-phonon line (ZPL) at 637 nm in diamond films. Fu et al[17] observed the polarization

of the emitted ZPL phonons as well as the ZPL linewidth is strongly temperature dependent, the local strain can be deduced from the orthogonal polarizations[1]. When the temperature is lower than 10K, the excitation spectrum of the NV^- reveals a fine structure of the ZPL that is highly dependent on strain[18] and electric fields[13]. There is no doubt that the local strain in diamond is related to the crystal structures, the internal defects as well as the growing conditions.

In this report, we investigate the temperature dependence of the spectral properties of various color centers in diamonds grown in several different ways. Measuring their photoluminescence (PL) spectra, we provide detailed characterization of the ZPL emission in the presented samples and discuss their differences.

Experimental Methods

Physical properties of the tested samples are summarized in Table.1. We chose three types of polished Diamond samples labeled as CVD, Natural and HPHT-treated natural, and investigate their various optical properties.

Table.1 Samples used in the low temperature experiments

Samples	Description	Carat	Color / Clarity	Diamond Type
CVD1	CVD	0.30	H / VS2	IIa
CVD2	CVD	0.30	G / SI1	IIa
CVD3	CVD	0.31	Very light Gray / VS1	IIa
Natural1	Natural	0.41	H / VS2	IIa
Natural2	Natural	0.36	I / VVS1	IaAB
HPHT-treated	HPHT-treated natural	0.31	Light Brown / VVS2	IaAB

CVD1 CVD2 CVD3 Natural1 Natural2 HPHT-treated

The low temperature study was performed in the Montana Cryo-optic X-plane system. The sample was mounted on a customized sample adapter and then fixed to the Montana's sample chamber. The sample is thermally isolated from that of the xyz stage in the chamber, which reduces the position variation of the sample due to the temperature fluctuations. The measurements in this manuscript were performed in the temperature range was from 4K to room temperature with an interval of about 30K. The waiting time for each temperature point was 45-60 min to ensure that the sample temperature is stabilized and reaches the temperature value set by ATSM controller. Sketch of the experiment setup is shown in Fig.1. The fiber coupled laser at 514.5 nm (~15 mW) was used to excite samples, using a high numerical aperture microscope objective lens (N.A.=0.85). The photoluminescence (and Raman) signal were collected by the same lens, coupled into a multimode fiber, and analyzed by a computer controlled Andor spectrograph with a CCD detector. The laser was operational only when the spectrum was collected in order to reduce the laser induced heating effects. The narrowest slit was used at the input of the spectrograph (10um) to reduce the effect of the line profile broadening by the monochromator. This allows us to determine the temperature dependence of the ZPL parameters such as peak position with full width at halr lf maximum (FWHM).

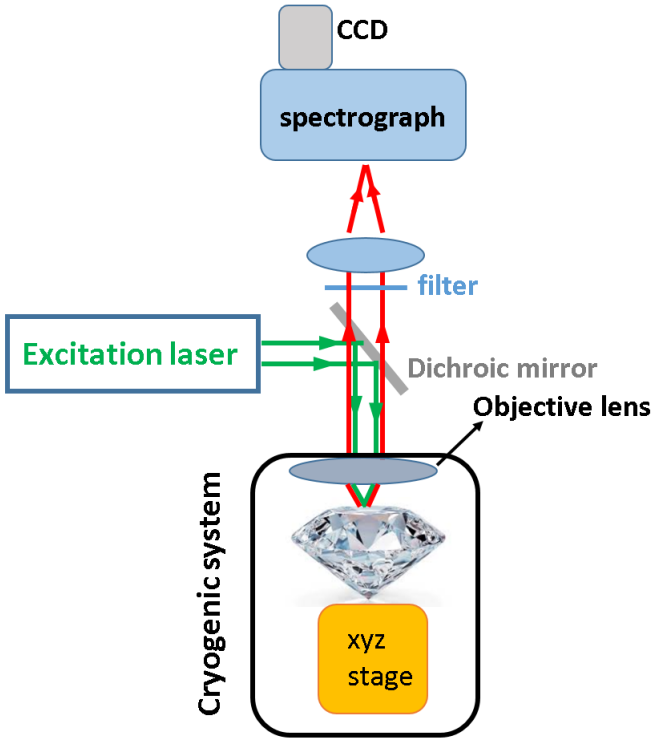


Fig. 1 Sketch of the experimental setup

Result and Discussion

Fig. 2 shows the PL spectra collected at the cryogenic and room temperatures from the diamonds containing NV centers. At room temperature, the CVD diamonds and HPHT-treated diamond had a broad band emission, covering 550 - 780nm (Fig.2a-2c) and 600 - 800nm (Fig.2d) range, respectively, while the emission of the natural diamond was centered below 550nm (Fig.2e-2f). At low temperatures, sharp and strong ZPL emission of NV^0 and NV^- centers were observed, as expected, compared to the room temperature results. Emission from Silicon-related defect at ~736nm was observed in the case of the three CVD grown samples (Fig.2a-Fig.2c) at low temperature. The 694nm peak accompanied by the relatively strong 637nm emission of NV^- center in Fig.2d is assigned as Ni-related center[19], and is commonly observed in HPHT-treated diamond. The 700 nm emission (Fig.2f) was also observed in HPHT treated diamonds. Previously, it was noted that the enhanced emission at this wavelength is especially pronounced in brown type Ia diamonds HPHT-treated at a temperature of 2000 ^oC. [19] The very strong NV^- at 636nm and the almost invisible NV^0 at 574nm peaks in HPHT-treated sample (shown in 2d) are believed that HPHT treatment increases the NV^- and decrease the NV^0 concentration[19].

Previously, it was reported the 588 nm (587 nm at low temperature) center is frequently observed in PL spectra of the nitrogen-containing and/or Ni-containing HPHT-treated natural diamonds[19]. The GR1 center(741nm) along with the 535 and 588 nm centers are common features of the diamonds which were processed by HPHT annealing followed by the electron irradiation and final annealing at temperatures below 800 ^oC. Therefore, the weak 575 nm emission, and strong 636 nm and 588 nm emission, along with the 740 nm peaks shown in “Natural 2” (Fig.2f) were consistent with previously observed color centers of the diamond that went through multi-process treatment. [19]

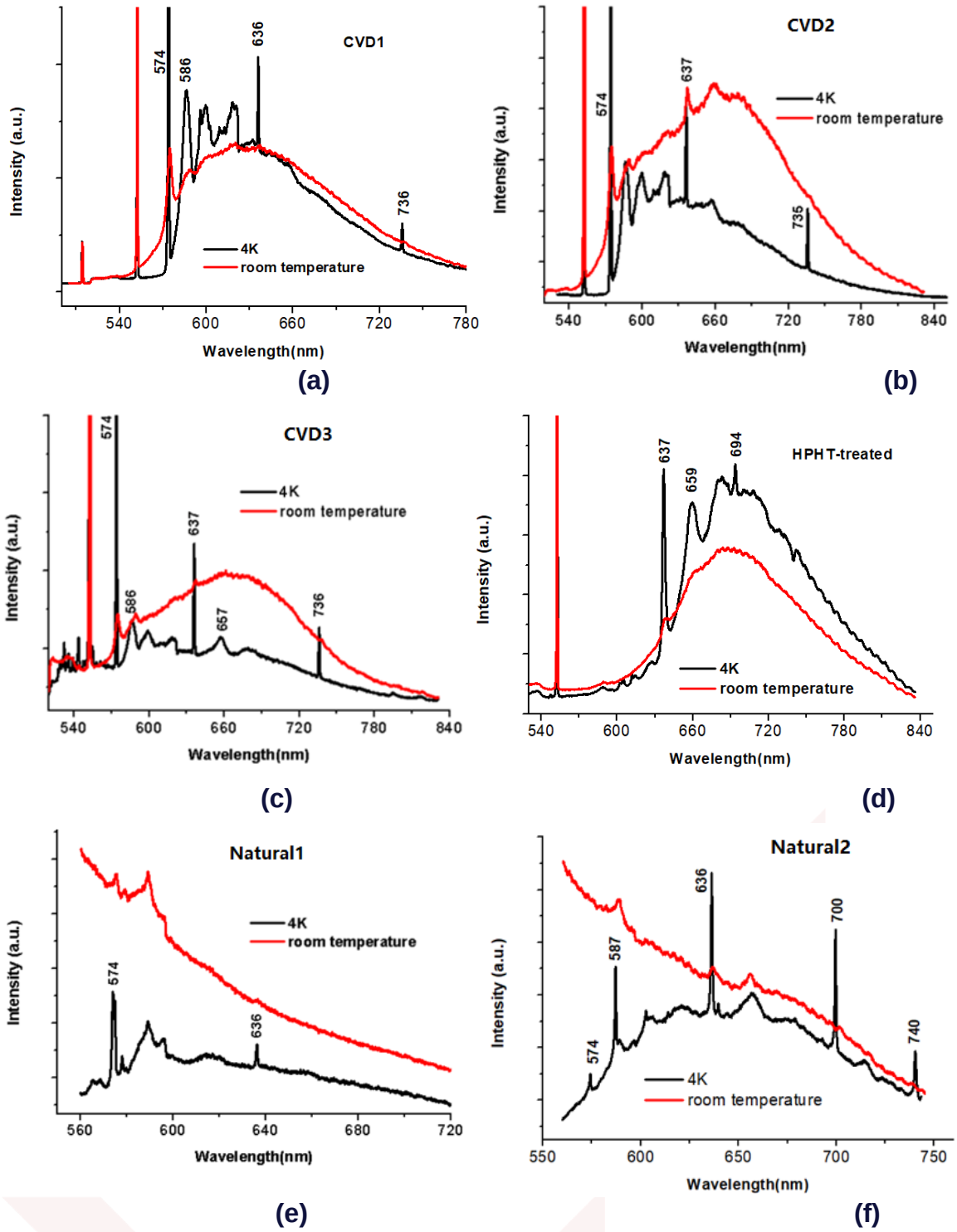
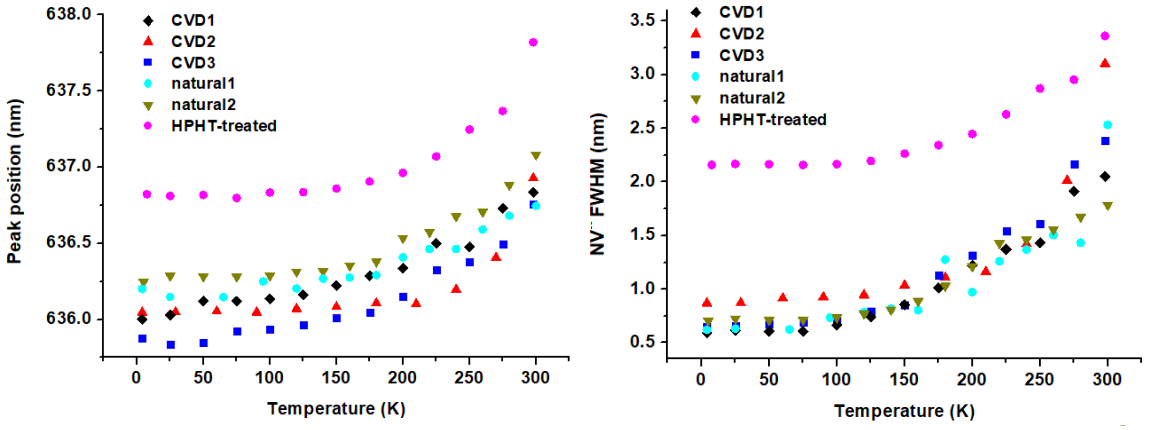


Fig.2 PL spectra of diamond samples form Table 1. at room temperature and 4K

By comparison of the data presented in Fig.2, the intense ZPL of NV^- at low temperature is shown in all samples studied. Due to its smaller width, blue shift was also observed with decreasing temperature. ZPL width was sensitive to lattice dislocations in diamond, widening

with increased local strain[20]. In order to study temperature dependent ZPL properties of the NV^- center, we fitted the 637 nm peaks measured at different temperatures with Lorentz distribution for all the studied samples. Peak position and FWHM were deduced from fitting curves and are shown in Fig.3. A red shift and broadening of ZPLs are clearly observed when the temperature is increased from 4K to room temperature (~300K). Both ZPL energies and FWHM depend nonlinearly on temperature and tend to be stable at low temperature, which is consistent well with observation of Chen et al.[21] The FWHM of NV^- for the diamonds was broadened about 1.5 nm from 4K to room temperature, which is in agreement with observations reported by Abtew et al [2,4].

Another noteworthy point in Fig.3 was that both the peak position and the FWHM of NV- from HPHT treated sample were higher than those of the CVD and Natural samples. While it has been reported previously that the HPHT treatment increases the internal strain in the vicinity of the NV defects[19], the results indicates that more detailed research study is worth to conduct for explaining this effect in the future.



(a) NV^- ZPL peak position (b) NV^- ZPL linewidth (FWHM)

Fig.3 Temperature dependent ZPL properties of NV^- center

Conclusion

In this work, the temperature dependence of the spectral properties of several diamond defects has been investigated for diamonds grown using various techniques. Measuring diamond photoluminescence spectra enabled identifying the nature of these defects and provided a more comprehensive understanding of the NV- defect properties at different temperature regimes and in different diamond hosts.

About the Authors

Dr. J. Cheng is Principal Engineer (expertise in Optical Spectroscopy), Dr. S.C. SHAM is Technical Supervisor, Mr. K.W. Cheng is Technical Manager and Mr. Tony K.C. Hui is Senior Director of the NanoTechnology Development & Applications Centre (NTAC), at Master Dynamic Limited in Hong Kong.

Dr. Stefan Bogdanovic is Postdoctoral Fellow in Applied Physics and Dr. Marko Loncar is the Tiantsai Lin Professor of Electrical Engineering, both at Harvard University.

References

1. Manson, N.B. and e. al., *Assignment of the NV0 575 nm zero-phonon line in diamond to a 2E-2A2 transition.* 2013.
2. Robledo, L. and e. al., *Control and Coherence of the Optical Transition of Single Nitrogen Vacancy Centers in Diamond.* Phys. Rev. Lett., 2010. **105**.
3. Fu, K.-M.C., et al., *Conversion of neutral nitrogen-vacancy centers to negatively charged nitrogen-vacancy centers through selective oxidation.* Appl. Phys. Lett., 2010. **96**.
4. Abtew, T.A., Y.Y.Sun, and e. al., *Dynamic Jahn-Teller Effect in the NV Center in Diamond.* Phys. Rev. Lett., 2011. **107**.
5. Häußler, S. and e. al., *Photoluminescence excitation spectroscopy of SiV− and GeV− color center in diamond.* New Journal of Physics, 2017. **19**: p. 063036.
6. Dragounov´, K.r. and e. al., *Determination of temperature dependent parameters of zero-phonon line in photo-luminescence spectrum of silicon-vacancy centre in CVD diamond thin films.* Journal of Electrical Engineering, 2017. **68**.
7. Waldermann, F.C. and e. al., *Creating diamond color centers for quantum optical applications.* Diam. Relat. Mater., 2007. **16**.
8. Togan, E., Y.Chu, and e. al., *Quantum entanglement between an optical photon and a solid-state spin qubit.* Nature, 2010. **466**.
9. G, B. and e. al., *Ultralong spin coherence time in isotopically engineered diamond.* Nat Mater., 2009. **8**.
10. Schirhagl, R., K. Chang, and e. al., *nitrogen-vacancycenters in diamond: nanoscale sensors for physics and biology.* Annu. Rev. Phys. Chem, 2014. **65**: p. 83.
11. Childress, L. and R. Hanson, *Diamond NV centers for quantum computing and quantum networks.* MRS Bull., 2013. **38**: p. 134-138.
12. *http://pettagroup.princeton.edu/nvs.html.*
13. Ph, T., et al., *Spin-flip and spin-conserving optical transitions of the nitrogen-vacancy centre in diamond.* New Journal of Physics, 2008. **10**(4): p. 045004.
14. Jelezko, F., I. Popa, and e. al., *Single spin states in a defect center resolved by optical spectroscopy.* Appl. Phys. Lett., 2002. **81**.
15. Dräbenstedt, A., et al., *Low-temperature microscopy and spectroscopy on single defect centers in diamond.* Physical Review B, 1999. **60**(16): p. 11503-11508.
16. Hizhnyakov, V. and V. Boltrushko, *Strong Jahn–Teller effect in the excited state: Anomalous temperaturedependence of the zero-phonon line.* J. Chem. Phys., 2003. **119**.
17. Fu, K.-M.C. and e. al., *Observation of the Dynamic Jahn-Teller Effect in the Excited States of Nitrogen-Vacancy Centers in Diamond.* Phys. Rev. B, 2009. **103**: p. 256404.
18. Batalov, A. and e. al., *Low temperature studies of the excited-state structure of negatively-charged nitrogen-vacancy color centres in diamond.* 2009.
19. Dobrinets, I.A. and e. al., *HPHT treated diamonds*. 2013: Springer Series in Materials Science.
20. Wang, W., et al., *CVD synthetic diamonds from Gemesis Corp.* GEMS&GEMOLOGY, 2012. **Summer**: p. 80.
21. Dohety, M.W. and e. al., *Temperature shifts of the resonances of the NV- center in diamond.* Phys. Rev. B, 2014. **90**: p. 04120.