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Photoluminescence of Point Defects in Diamond relevant to Quantum Information Processing

M.D. Sastry*

Gemmological Institute of India, 304, Sukhsagar Building, Opera House, Mumbai-400 007

Abstract
The paper describes the photoluminescence of centres in Diamond which have been found to be suitable as single photon emitters. It is remarkable that at least four centres in diamond viz NV- , SV-, NE8 (Ni coordinated to four nearest neighbour nitrogens) and a green emitting centre, are found to be suitable as single photon emitters at room temperature, which have the potential to be used for quantum Information processing (QIP). The main reason for this seems to be due to high Debye temperature of diamond resulting in intense zero phonon lines at room temperature. Results are presented on the luminescence of three of the four centres mentioned. The NV- colour centres are produced by electron beam treatment and subsequent heat treatment. The electronic configuration of NV- makes it paramagnetic both in the ground and excited states; the allowed transition being the triplet to triplet with possibility of intersystem cross over to singlet state. Some recent work reported in literature on this centre for single photon emission are also presented.

1.INTRODUCTION

Impurity centres introduced either by chemical doping or by radiation treatment generally in the range of a few ppm to a few hundred ppm, play a crucial role in the colouration and luminescence properties of colourless insulating materials[1]. High resolution spectroscopy of defects in solids like fluorescence line narrowing, hole drilling spectroscopy made it possible to investigate the electron-nuclear hyperfine interactions including quadrupole interaction using optical methods. These studies could also come under the general category of optically detected magnetic resonance (ODMR); having the advantage of high sensitivity of optical excitation/detection and high resolution of microwave/radiofrequency spectroscopy. In most of the cases the electron – vibration interaction results in large Stokes' shift in the Photoluminescence of point defects which leads to a wide vibronic component in fluorescence. This process is preceded by a wide vibronic absorption band during excitation [2]. The vibronic part of the emission/ absorption spectrum is not useful for ODMR studies. With lowering of temperature the vibronic part of the spectrum goes down in intensity with concomitant increase in the intensity of zero phonon line (ZPL) which is a pure electronic transition. Pure electronic transitions only are amenable for investigating electron- nuclear coupled and other quantum entangled states which are a basic requirement for quantum information processing (QIP)[3]. The intensity of ZPL reflects the strength of electron-vibration interaction; more the strength of interaction lesser being the intensity of ZPL. For zero phonon emission apart from the orbital degeneracy of the electronic states, the phonon density of states plays an important role; lesser the density of vibrational states lesser the strength of electron-vibrational interaction. Therefore, apriori one would expect more intense ZPL in solids with higher Debye temperature. This leads one to expect the photoluminescence of point defects in diamonds, the hardest material with large Debye temperature of 2220K, to display prominent ZPL[5].

Coloration of diamond by electron beam treatment (EBT), ion implantation or by fast neutron irradation [6] is dominated by the production of carbon vacancy which is not a void but contains four electrons distributed over four dangling bonds of the neighboring carbon atoms. Carbon vacancies have strong affinity to nitrogen impurity forming a variety of nitrogen-vacancy complexes. The presence of carbon vacancies imparts blue colour to diamonds. When type II diamond with very low concentration of nitrogen is heated beyond 800C after EBT, the vacancy becomes mobile and forms nitrogen-vacancy centre (NV centre), with ZPL at 575nm, on getting closer to a nitrogen defect. Such a centre easily traps an electron forming NV^- centre with ZPL at 637nm. This centre was found to be highly stable, strongly fluorescing and optically un bleachable. This centre has served as archetypal centre for single photon emission and quantum information processing [3,7-11]. There are at least three other centres in diamond

* Corresponding author: E-mail: mdsastry@yahoo.co.in
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which were found to be satisfactory for quantum information processing. These are SiV, NE8 (Ni at carbon site bonded to four nitrogens at the nearest neighbour carbon sites) and an unidentified green emitting centre at 532nm. The PL properties of these centres obtained in authors laboratory are presented.

Nitrogen- vacancy complexes in Diamond

We [12,13] investigated six natural diamond samples, e-beam irradiated to a cumulative dose of 10^{18} e per sq cm. Except for one sample , other samples were heat treated . Unheated sample (designated as sample-E) was blue , and the heat treated samples (three in number) were coloured pink (sample-F), purple (sample-G), and lemon-yellow(sample-H).

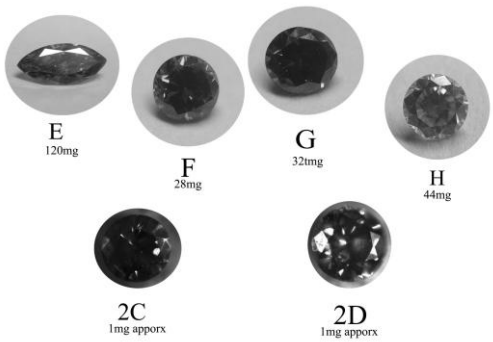

Fig.1 : Electron beam treated (EBT)diamonds. Diamonds E,2C,2D were not heated subsequent to EBT where as the others (F,G,H) were heated to 800-1200C.

Absorption spectra of these samples were taken at room temperature and 77K, using a Varian-Cary 5000 spectrophotometer. All the samples yielded only weak and noisy fluorescence on 240nm UV excitation. Excitation in the visible region resulted in intense fluorescence and the relative intensities were dependent on the excitation wave length. Before heat treatment all the diamond crystals were blue due to formation of carbon vacancies which exhibit wide absorption with ZPL at 741nm extending to 500 nm. This causes blue colour on electron beam treatment of diamonds. Laser excited PL studies using 325,514 and 785 nm excitations were carried out. Figure 2 shows a PL spectra of the samples with 514nm excitation. It may be seen that NV^- centre, with ZPL at 637nm, develops only after irradiation and heat treatment.

NV^- Centre (ZPL at 637 nm) and SiV (ZPL at 738nm) centres

Centres NV-, SiV, a green emitter center at 532nm and a nickel centre with ZPL at 800nm are of interest as single photon emitters for quantum cryptography [10]. Amongst these, the NV- centres can be produced more easily. The nitrogen- vacancy centres are formed in electron beam treated/ fast neutron irradiated diamonds and when heated to 800-100C temperature the vacancy becomes mobile and forms a complex with isolated nitrogens at lattice position.

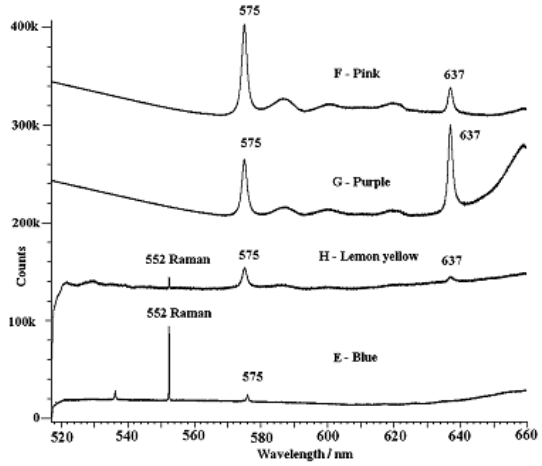

Fig 2: Photo luminescence of diamonds E,F,G,H under 514nm excitation. The evolution of NV (ZPL 575 nm)and NV- (ZPL 637 nm) can be seen

When such a sample with isolated nitrogens is subjected to HPHT treatment, nitrogen transfers an electron to a neutral NV centre transforming a NV^- centre. This centre containing two unpaired electrons is paramagnetic with ^3A as the ground state. Its first excited state is ^1A and the next excited state is ^3E. The transition from ^3E to ^3A is spin allowed and results in 637 nm (1.952 eV) ZPL emission. The schematic energy level diagram is shown in Figure 7.

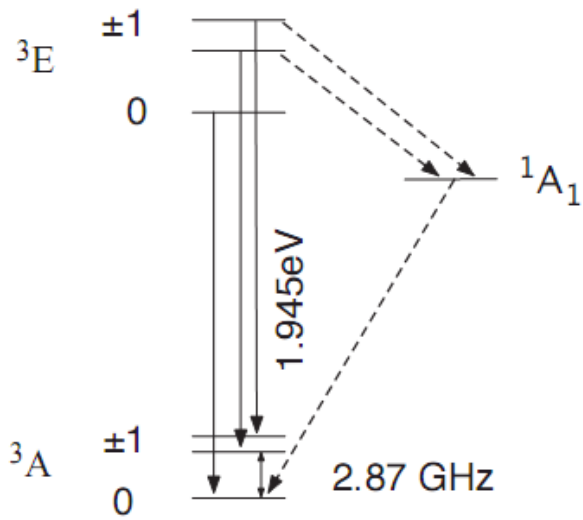

Fig 3: Energy level diagram 0f NV- centre. Transition between ground state 3A and excited 3E states is spin allowed ; resulting in 637nm ZPL. Intersystem crossing via 1A does not give the fluorescence. The intensity of PL is affected by changing the population of Ms =0 and ±1 sub levels in the ground state by microwave excitation at 2.87 GHz[3]. The fluorescence life time of Ms = ±1 sub levels is 7ns and of Ms =0 sub level is 11ns[10]

This centre has been the subject of interesting PL studies both in bulk and at nanoscale diamonds. This centre had shown high photo stability. Microwave-Optical double resonance experiments were used r to detect Optically detected electron spin resonance (ODESR). This became possible due to intersystem cross over to the dark ^{1}A state from the excited ^{3}E state. The hyperfine interactions with ^{14}N and ^{13}C nuclei were also well resolved in ODESR.

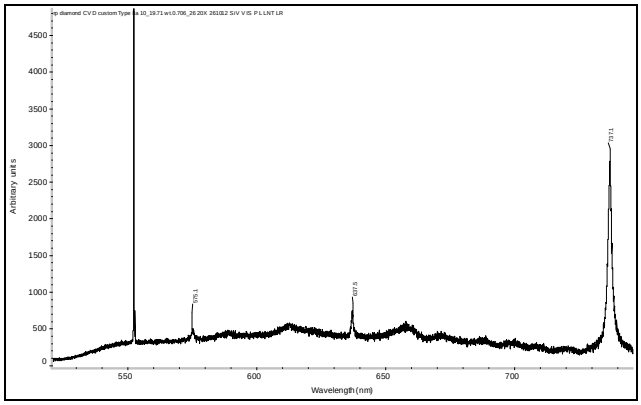

Fig 3: The PL spectrum of a CVD diamond at 77K. Excitation is at 514nm

SiV centre with ZPL at 738nm is an equally interesting centre and is more commonly observed in CVD grown diamonds. Si does not take exactly the lattice position in diamond and weakly interacts with the lattice; this results in smaller ground state splitting and a weak electron phonon interaction unlike NV-. This increases the yield of ZPL even at room temperature with shorter (4ns) life time compared to NV- (13ns). A typical PL spectrum of a CVD diamond, excited with 514nm laser, is shown in Figure 4. This was obtained in authors' laboratory. The ZPL of NE8 centre, nickel ion coordinated to four first neighbor nitrogens, is another promising centre for single photon emission. The temperature dependence of ZPL of of NE8 is shown in figure 4.

The Photoluminescence and ODMR measurements are normally done using confocal Raman/PL spectrometers wherein the diffraction limited laser spot size on the sample is no more than a micron cube. In samples in which the radiation induced defects are not more than 10^{12} per c.c ; the concentration of the luminescent defect of interest in the laser spot volume of one cubic micron at any random position would be 0,1 or 2 the most probable being 1. If the emission arises from only one centre one woud be dealing with a single photon emission. Neuman et al [10] have resolved dipolar interaction between two NV- centres separated by 10nm; using the differences in fluorescence life time of transitions connecting different spin sublevels. Number of workers have ascertained that the PL is arising from only one NV- centre by measururing second order auto correlation function $g^{(2)}$of PL photons at 637nm; its value going to zero at t=0 proving the involvement of single defect associated with single photon emission. Similar measurements were done with SiV- and NE8 centres. Recently Smith et al [9] have shown that a green emitter at 532nm is potentially promising single photon emitter as it has a high Huang- Rhys factor and low fluorescence life time. The relevant data on all known single photon emitters is summarized in Table 1.

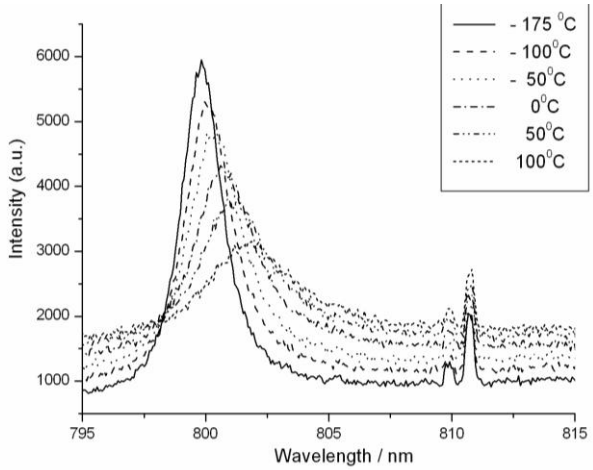

Fig 4 : Temperature dependence of ZPL of NE* centre in Diamond 2D.

Table 4 : ZPL data of some of the single photon emitters in diamond (ref10)

ZPL details	**532**	**NV-**	**SiV-**	**NE8**
Wave length (nm)	532	637	738	800
Line Width	0.8	2	0.7- 4.9	2
Huang-Rhyes factor	2.48	3.2	0.2	0.4
Life time (ns)	3.3	12.6	2	11.5

In summary, a brief exposure is given about the potential of fluorescence and ODMR studies of colour centres in diamond at room temperature. We have observed all the centres in PL at room temperature; but quite far from reaching the stage of single photon detection and to QIP applications. In the context of luminescence research in India there is a lot of scope and requirement for initiating work on fluorescence microscopy with a view to achieving single photon emission and detection; be it in diamond or organic molecules of biological interest.

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