Fluorescent Nanodiamonds with Silicon-Vacancy Color Center: A Potential Cellular Biolabels

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ABSTRACT

The effect of particle size as well as the nitrogen content in the feedgas on room temperature photoluminescence of nanodiamonds, discrete nanodiamond particles of averaged size 500nm, 250nm, 100nm and 6nm were dispersed on to silicon substrate and plasma treated using microwave plasma chemical vapor deposition to create silicon vacancy color centers. We observed that adding nitrogen in feedgas increased the intensity of silicon vacancy color center room temperature photoluminescence. The resulting narrowband room temperature photoluminescence is intense, and clearly observed even for weakly agglomerated sub-10 nm size diamond. This is in contrast to the well-studied nitrogen-vacancy center in diamond which has luminescence properties that are strongly dependant on particle size, with low probability for incorporation of centers in sub-10 nm crystals. We suggest the silicon-vacancy center to be a viable alternative to nitrogen vacancy defects for use as a biolabel in the clinically-relevant sub-10 nm size regime.

Keywords: fluorescence nanodiamonds (FND), room temperature photoluminescence, silicon vacancy color centers, nitrogen vacancy color centers, microwave plasma chemical vapor deposition (MPCVD).

1 INTRODUCTION

Conventional fluorophores based on organic dyes or proteins have been intensively used in biological labeling. However, they have apparent limitations as a result of photobleaching (brightness fading) for time dependent study of in vitro or in vivo processes. Semiconductor nanocrystal 'quantum dots' (QD) have much higher photobleaching thresholds[1]. However, surface modifications are often necessary to reduce toxicity and to increase water solubility [2], which inevitably changes their photophysical properties [1,3] . In addition, QD suffer from intermittency in their emission, called "blinking." Nanodiamond (ND) particles offer an emergent technology with one of its main applications as a perfectly photostable luminescent emitter upon incorporation of color centers, such as the predominantly studied negatively charged nitrogen-vacancy $(NV)^-$ defect [4] . The majority of studies on ND have revealed low cytotoxicity [5] and low animal toxicity [6], and have demonstrated that the surface can be easily modified with a wide range of functional groups to provide a versatile platform for conjugation with small molecules, proteins, and nucleic acids [7] . These properties have led to intense interest in ND not only as an imaging probe, but also as a drug and gene delivery platform. The ability to produce and detect N-V centers in isolated sub - 10 nm nanodiamonds is strongly debated, and skepticism remains as to their stability as a useful emitter in a discrete crystal. Density functional tight binding simulations predict the preferable positioning of nitrogen as being at the surface of nanodiamonds, where formation of N-V defects is unlikely to occur [8]. This also supports predictions that N-V centers are not present in nanodiamonds smaller than 10 nm [9] . Very recently, N-V centers in discrete 5 nm ND was reported, although luminescence blinking was observed [4]. Since the nitrogen-vacancy (N-V) center in diamond has luminescence properties that are strongly dependant on particle size with low probability for incorporation of centers in sub-10 nm crystals, Silicon vacancy color center emerged as an alternative because of its numerous promisng emission properties Such its sharp zero phonon line (FWHM of about 5 nm) at 738 nm and short fluorescence lifetime of about 2 ns (compared to 13 ns for N-V center) [10, 11,] which is well separated from the characteristic broad band PL of ND (spread between 450nm and 650 nm), whereas the 637 nm ZP emission from $N\text{-}V^-$ defects overlaps ND PL. Since the silicon atom enters the diamond lattice interstitially and sits in the center of a split vacancy, this center does not couple strongly with the diamond phonons (in contrast to N-V center). The result is a relatively narrow fluorescence spectrum with a sharp zero phonon line, and a relatively weak phonon side band [12]. Thus, Silicon vacancy beacome a prominent candidate for efficient single photon source, but it also has great potential as a biolabel that has not yet been realized. Silicon vacancy (SiV) has been investigated in the form of thin chemical vapor deposited (CVD) films [8,13] but not in the form of isolated nanocrystals which are particularly relevant as biolabels or as a drug-delivery platform. In our experiments discrete nanodiamond (ND) particles with average size of ~6 nm were microwave plasma treated on silicon substrates in a Chemical vapor deposition (CVD) reactor to create silicon-vacancy centers. Our results represent that SiV incorporated in NDs readily exhibits strong narrow band room temperature fluorescence, even for sub-10 nm size particles in contrast to the well-studied nitrogen-vacancy center (N-V) in diamond which are reported to be relatively unstable and have particle size dependant luminescence properties, with low probability for incorporation of centers in sub-10 nm crystals.

2 EXPERIMENTAL DETAILS

The Si-V defect centers were created in ND particles seeded onto *n*-type (100) silicon substrates. The seeded substrates were exposed to a microwave plasma CVD process using 0.7% methane in hydrogen feedgas mixture, 820 ^{o}C substrate temperature, 40 Torr chamber pressure, and 0.85 kW microwave power. Silicon is efficiently etched in the hydrogen-rich plasma and redeposited with diamond to form the defect center. Two types of synthetic powders used were: (1) high-pressure high-temperature diamond milled to an average particle size of ~100nm, ~250 nm and ~500 nm as received from Electron Microscopy Sciences, and (2) explosion synthesized diamond with average particle size of 6 nm and purity of >98% from Nanostructured and Amorphous Materials, Inc. We also added 0.025 % and 0.04% nitrogen in hydrogen feedgas with 0.7% methane, keeping all the other parameters same as in case of without nitrogen, to determine the effect of nitrogen addition on silicon vacancy color center formation. In order to confirm the presence of Si-V and NV defects, room temperature photoluminescence (PL) spectroscopy (excitation wavelength of 532 nm) was performed on pre- and post- CVD treated ND particles on the silicon substrates respectively [14].

3 RESULTS

SiV color centers offer several promising aspects such as the stable narrow fluorescence spectrum at room temperature for sub -10 nm diamonds and short luminescence lifetime. However, relatively low brightness of the SiV centers in diamond revealed a poor quantum yield. The local atomic environment around a Si-V center is expected to influence photon emission characteristics, especially if it results in substantial non-radiative transitions. SiV centers have non-fluorescing charge states as in case of natural semiconducting diamond with negligible nitrogen content, the luminescence of SiV centers was not detectable. However, by manipulating the occupancy of the charge states with a high concentration of isolated nitrogen, photoluminescence of SiV centers ~ 738 nm can be found to be relatively more intense. The isolated nitrogen atoms that act as donors in diamond and raise the Fermi-level to a position near the conduction band. The SiV center has a more positively charged state, which is not optically active. With higher position of the Fermi-level, the fraction of SiV centers in the optically inactive charge state becomes smaller hence the effect of correlated emission is reduced as a result, the emission of SiV centers increases. An optically inactive charge state can provide a channel for nonradiative transitions. SiV center has ground state energy at E_c−2.05 eV, which results in an excited state close to the conduction band, making photothermal ionization possible. If the SiV center loses an electron, it becomes positively charged thus, incapable of photon emission. Positively charged state has energy E_v + 2.5 eV. Therefore, the positively charged state can be regarded as the "shelving level" in the three-level model. Thus, we can conclude that the structure of SiV together with nitrogen doping will enhance its luminescence properties. This is in agreement with observations that no Si-V luminescence was detectable in sub -10 nm diamond having negligible nitrogen content. This suggests the possibility of enhancing Si-V emission in ND through controlled nitrogen doping [15] .

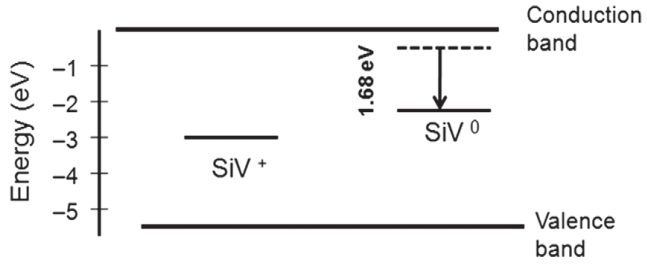

Fig 1: Schematic showing the position of charge states for Si-V center in the band gap. The positively charged Si-V state is optically inactive.

Figure 2 shows Room temperature PL spectra of 6nm, 100nm, 250nm and 500nm ND averaged size particles without Nitrogen in the feedgas of hydrogen with 0.7% methane. PL for 6nm is very broad and characteristic peak related to silicon vacancy color center is almost vanished while nitrogen vacancy color center characteristic peak is more intense. SiV color center characteristic peak becoming more prominent as particles size increases 6nm to 250nm.

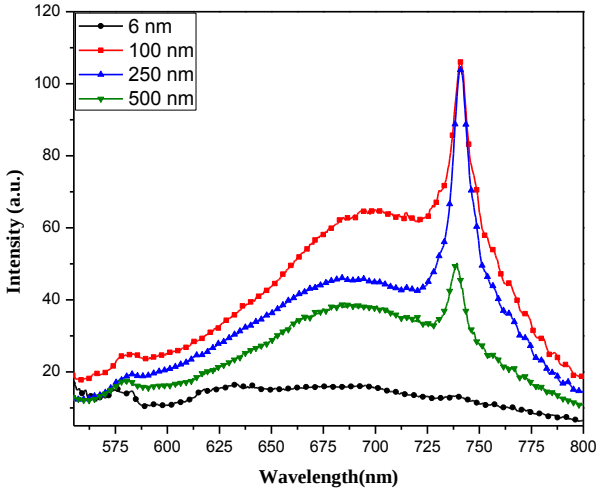

Fig 2: Photoluminescence spectra of post-CVD treated 6nm, 100 nm , 250nm, and 500 nm ND seeded onto silicon substrates without nitrogen in feedgas. A strong and narrow zero-phonon line at 738 nm is accompanied by a weak phonon side-band at 757 nm is observered except 6 nm ND.

Figure 3 shows Room temperature PL spectra of 6nm, 100nm, 250nm and 500nm ND averaged size particles with N_2 = 0.04% in the feedgas of hydrogen with 0.7% methane. PL for 6nm is broad and the intensity of the characteristic peak related to silicon vacancy color center is very intense (compared to without nitrogen case) while nitrogen vacancy color center characteristic peak is more intense compared to other particles sizes. Also, as particles size increasing from 6 nm to 250nm, Si V characteristic peak becoming more prominent but decreased for 500nm.

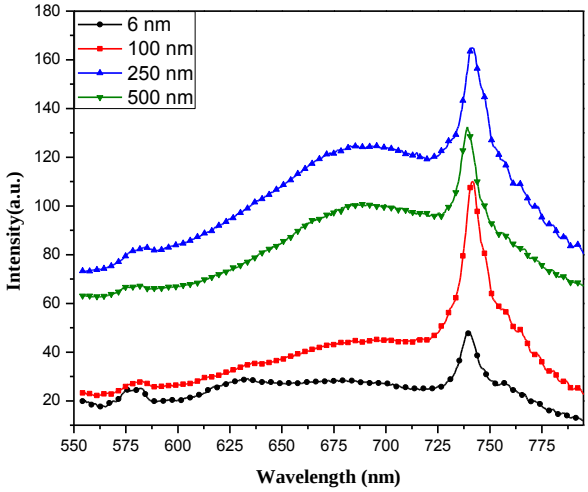

Fig 3: Photoluminescence spectra of post-CVD treated 6nm, 100 nm , 250nm and 500 nm ND seeded onto silicon substrates with N_2 = 0.025% and 0.04 % in feedgas. A strong and narrow zero-phonon line at 738 nm is accompanied by a weak phonon side-band at 757 nm is observered even for 6 nm ND.

Figure 4 shows Room temperature PL spectra of CVD plasma treated 6nm averaged size particles with N_2=0.025% and 0.04% and without Nitrogen in the feedgas of hydrogen with 0.7% metahne. PL is very broad and characteristic peak related to silicon vacancy color center is almost vanished while nitrogen vacancy color center characteristic peak is intense in case of without N_2. With N_2 = 0.025% in the feedgas SiV characteristic peak intensity become visible while NV characteristic peak intensity decreased slightly compared to without N_2 case. N_2 =0.04 % intensity of SiV color center became sharp. PL spectra of preCVD sample is also plotted which shows no sign of SiV or NV.We also verified the relative intensity of SiV and N-V color centers by using Gaussian peak fitting and approximated the area under the peak. The histrogram shows that increasing the nitrogen content in the feedgas of hydrogen with 0.7% methane, room temperature photoluminescen of silicon vacancy color center become prominent and sharp.

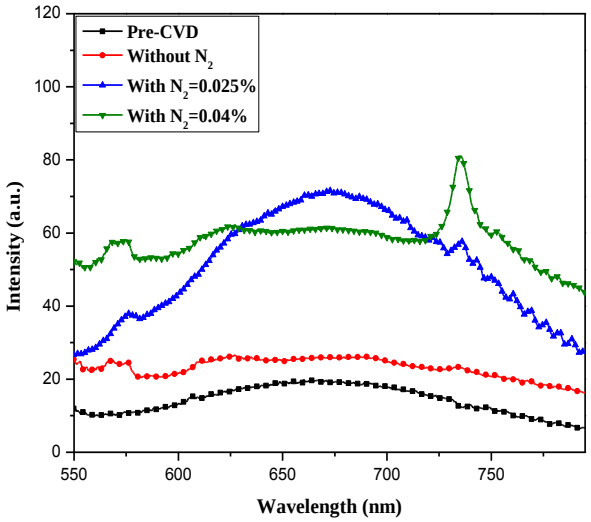

Fig 4: Photoluminescence spectra of pre- and post-CVD treated 6nm ND seeded onto silicon substrates without nitrogen and with N_2 =0.025% and 0.04% in feed gas. A strong and narrow zero-phonon line at 738 nm accompanied by a weak phonon side-band at 757 nm is observed in case of N_2=0.04%.

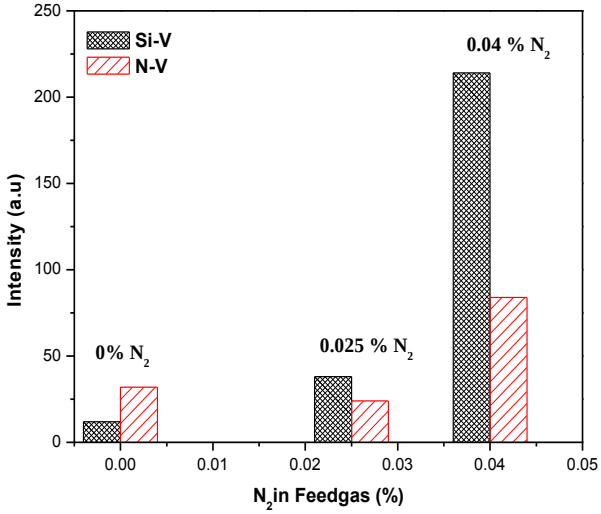

Fig 5: relative intensity of Room temperature photoluminescence associated with silicon and nitrogen vacancy color centers for 0%, 0.025% and 0.04 % Nitrogen in hydrogen feedgas with 0.7 % methane. Increased amount of Nitrogen enhanced the intensity of Silicon vacancy color centers for sub-10 nanometer discrete nanodiamonds.

4 CONCLUSION

In summary, discrete nanodiamond particles with average size of 6 nm, 100nm, 250nm and 500 nm were microwave plasma treated on silicon substrates in a CVD reactor to create silicon-vacancy centers. The resulting nanodiamonds clearly exhibit strong narrow band

fluorescence, even for sub-10 nm size particles. The characteristic room temperature photoluminescence of nitrogen vacancy color center is present in all the Plasma treated samples except 6nm detonation NDs by using CVD even without any nitrogen incorporation in the feedgas of hydrogen with methane. The origin for this peak in large ND particles is associated with inherently present nitrogen in them. For 6 nm nanodiamonds there is a visible competition between SiV and NV color centers room temperature PL intensity. PL is very broad and characteristic peak related to silicon vacancy color center is almost vanished while nitrogen vacancy color center characteristic peak associated with NV^o is intense without even without N_2. Nitrogen vacancy PL peak is present in all the Plasma treated samples by using CVD even without any Nitrogen incorporation in the feed gas during the treatment. This may be because of the base pressure as it was not sufficiently low and had some nitrogen present in the CVD chamber. With N_2 = 0.025% in the feed gas SiV characteristic peak intensity become visible while NV characteristic peak intensity decreased slightly compared to without N_2 case. Adding N_2 = 0.04 % in feedgas of hydrogen with 0.7 % methane room temperature photoluminescence of SiV color center became very intense. As particles size in increases from 6 nm to 250nm, Si V characteristic peak becomes more prominent in both cases with and without nitrogen in feedgas but decreased for 500 nm that infer the optimum limit for ND particle size to get intense fluorescence . Thus, the enhancement of Si-V emission in diamond nanocrystals can be achieved through controlled doping of nitrogen, which can increase the Fermi level, reducing population of the positively-charge optically-inactive Si-V state, and thereby increase emission from Si-V centers. The Si-V center offers a viable alternative to nitrogen-related defects as a fluorescent biolabel of clinically-relevant size, allowing accessibility to study biological processes which require enhanced luminescence at the sub-10 nm regime, for which nitrogen defect-related luminescent activity and stability is reportedly poor.

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