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Strong Narrow-Band Luminescence from Silicon-Vacancy Color Centers in Spatially Localized Sub-10 nm Nanodiamond

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Abstract

Discrete nanodiamond particles of 500 nm and 6 nm average size were seeded onto silicon substrates and plasma treated using chemical vapor deposition to create silicon-vacancy color centers. The resulting narrow-band room temperature photoluminescence is intense, and readily 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 biomarker in the clinically-relevant sub-10 nm size regime, for which nitrogen defect-related luminescent activity and stability is reportedly poor.

1. INTRODUCTION

While conventional fluorophores based on organic dyes or proteins have been the mainstay in biological labeling, their limitations become apparent when studying time-dependant *in vitro* or *in vivo* processes as a result of photobleaching (brightness fading). Semiconductor nanocrystal ‘quantum dots’ (QD) have much higher photobleaching thresholds and offer the possibility of multicolor staining by size tuning.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 that is gaining considerable attention 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 (N-V)[−] defect.⁴ The majority of studies on ND have revealed low cytotoxicity⁵ 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. In fact, ND has recently been utilized in a very diverse range of applications such as reinforcement in nanocomposites for achieving enhanced mechanical properties,⁸⁻¹⁰ as field electron emitters for high power devices,¹¹ and as a substrate for enhanced adhesion and growth of osteogenic cells.¹²

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.¹³ This also supports predictions that N-V centers are not present in nanodiamonds smaller than 10 nm.¹⁴ The improbable N-V emission for very small diamond nanocrystals, including the ~5 nm size made by detonation technique, has been experimentally confirmed by several investigators.¹⁵⁻¹⁷ Although N-V centers have been produced in sub-10 nm ND using a top-down approach by milling luminescent microdiamonds,¹⁶ the N-V stability in isolated detonation-produced ND is still in question. 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, the search for alternative ND-based emitters is underway. Only recently has the Si-V center gained attention as a single photon source due to 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).¹⁷⁻¹⁹ 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. Theoretical calculations have shown the Si-V complex to be the most stable configuration for Si-related defects,¹⁸ thus supporting experimental observations of enhanced luminescence properties compared diamond with N-V centers.^{17, 19} The significance of this is a relatively efficient single photon source, but it also has great potential as a biomarker that has not yet been realized. This defect has been reported in the form of thin chemical vapor deposited (CVD) diamond films^{17, 18} and ion-implanted single crystal diamond windows.¹⁹ In the case of CVD nanostructured diamond films with substantial amorphous carbon components, the surface Fermi level can be lowered closer to the valence band and reduce the population of defect states that could otherwise lead to photoluminescence.²⁰ In this paper, we demonstrate intense luminescence for discrete Si-V nanodiamonds in the sub-10 nm size range which is clinically relevant as biolabels or as a drug-delivery platform. To this end, the lower end of the nanoscale will be more accessible for study of biological processes requiring enhanced luminescence not currently provided by N-V centers in ND.

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 a 0.7% methane in hydrogen feedgas mixture, 800 °C substrate temperature, 40 Torr chamber pressure, and 775 W microwave power. Silicon is efficiently etched in the hydrogen-rich plasma and re-deposited 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 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. Room temperature photoluminescence (PL) spectroscopy (excitation wavelength of 532 nm) was performed on pre- and post-CVD treated ND particles on the silicon substrates in order to confirm the presence of Si-V defects, respectively. Atomic Force Microscopy (AFM; Nanoink DPN5000), Confocal Fluorescence Microscopy (CFM; Zeiss LSM 710), and Transmission Electron Microscopy (TEM; FEI Tecnai F20 FEG) was used to image nanodiamond particles after CVD treatment. For TEM sample preparation, post-CVD treated ND particles were mixed with bovine gelatin in 2,2,2-trifluoroethanol (TFE) and dried onto TEM grids to make a solid composite film containing 5% by weight of dispersed ND in gelatin. The CFM

measurements were collected using 543 nm excitation and an emission filter set between 708–758 nm in order to only collect light expected to be from the Si-V zero phonon line c.a. 738 nm.

3. RESULTS AND DISCUSSION

Figure 1 shows an AFM image taken on a ND-seeded silicon sub-strate post-CVD treatment for the case of seeding using explosion synthesized diamond particles of 6 nm average size. Localized regions on the substrate revealed isolated particles of uniform size averaging 9 ± 2 nm, with typical AFM line profile scans as shown in the inset of Figure 1 for the isolated particle indicated by the arrow. The short CVD deposition time of 10 minutes did not increase the ND particle size substantially from the initial average value of 6 nm. Fluorescence from discrete nanodiamond particles was confirmed using confocal fluorescence microscopy with emission collected between 708–758 nm to identify the Si-V centers. Figure 2 shows spatially localized red fluorescent emitters from the post-CVD treated 6 nm ND on silicon. Only weak agglomeration is evident and the intensity cross section of the smallest size observable emitters have bandwidths near the optical diffraction limit of about 300–400 nm. The observation of these diffraction-limited spots suggests that they are derived from isolated fluorescent NDs, some of which are likely to have the sub-10 nm size as measured in the AFM image of Figure 1. The post-CVD ND particle size was confirmed by TEM imaging of the ND/gelatin film (inset of Fig. 2), which shows uniformly sized sub-10 nm particles.

Figure 3 shows room temperature photoluminescence (PL) of the pre- and post-CVD treated ND particles on silicon for both 500 nm and 6 nm seeded particles. The PL spectra reveal narrow band emission c.a. 738 nm, characteristic of the zero phonon line of the Si-V center. The very strong and sharp (FWHM of ~ 7 nm) zero phonon line lies on a weak background fluorescence and weak phonon side band (c.a. 756 nm), even for the sub-10 nm size ND particles. This is in contrast to the N-V emission for similarly sized (5 nm) ND aggregates which have required high sensitivity time-gated PL spectroscopy to reveal a weak N-V signal from a strong luminescence background due to the eclipsing nature of graphitic surface layers.²¹ In our measurements, standard room temperature PL spectroscopy allowed observation of strongly luminescent Si-V defects for weakly agglomerated sub-10 nm ND particles.

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. Although the charge state of the Si-V center is predominantly neutral, PL quenching spectra have revealed the presence of a positively charged state located 2.5 eV above the valence band. The Si-V center can be modeled using a 3-level system in which the “shelving level” corresponds to the positively-charged, optically-inactive state as shown in Figure 4. In typical CVD diamond processes, background levels of nitrogen of only a tenth of one percent can result in significant nitrogen incorporation in diamond on the order of 15 ppm.²² In looking at the PL spectra of Figure 3, we see upon CVD treatment an increase in the very broad luminescence background c.a. 675 nm likely associated with nitrogen incorporation in ND. Isolated nitrogen atoms can act as donors and effectively pin the Fermi level closer to the conduction band. With an increased Fermi level caused by nitrogen doping, the population of the optically-inactive positively-charged state becomes smaller, and consequently the emission from Si-V centers increases. This is in agreement with observations that no Si-V luminescence was detectable in natural semi-conducting diamond having negligible nitrogen content.²³ This suggests the possibility of enhancing Si-V emission in ND further through controlled nitrogen doping.

4. CONCLUSIONS

In summary, discrete nanodiamond particles with average size of 500 nm and 6 nm were microwave plasma treated on silicon substrates in a CVD reactor to create silicon-vacancy centers. The resulting nanodiamonds readily exhibit strong narrow band fluorescence, even for sub-10 nm size particles. This represents a substantial improvement over similarly-sized nitrogen-vacancy centers which are reported to be relatively unstable and difficult to accommodate in sub-10 nm nanodiamond crystals. The potential for further enhancement of Si-V emission in diamond nanocrystals is suggested 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 biomarker of clinically-relevant size, allowing accessibility to study biological processes requiring enhanced luminescence at the sub-10 nm level.

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Fig. 1. Close contact AFM image of ND-seeded silicon substrate after CVD treatment to create Si-V centers for the case of seeding using explosion synthesized diamond particles of 6 nm average size. The inset shows a line profile across one of the particles (indicated by arrow) and reveals a particle size of 9 nm.

Fig. 2. Confocal fluorescence microscopy with emission collected between 708–758 nm to identify the Si-V centers from the post-CVD treated 6 nm seeded ND on silicon. Spatially localized red fluorescent emitters are observed with bandwidth near the diffraction limit of the microscope. The inset shows sub-10 nm average particle size, as imaged by TEM.

Fig. 3. Photoluminescence spectra of pre- and post-CVD treated ND seeded onto silicon substrates with average ND particle size of (a) 500 nm and (b) 6 nm. A strong and narrow zero-phonon line at 738 nm is accompanied by a weak phonon side-band at 757 nm.

Fig. 4. Schematic showing the position of charge states for Si-V center in the band gap. The positively charged Si-V state is optically inactive.