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Spatially Controlled Fabrication of Brightly Fluorescent Nanodiamond-Array with Enhanced Far-Red Si-V Luminescence

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Abstract

We demonstrate a novel approach to precise pattern fluorescent nanodiamond-arrays with enhanced far-red intense photostable luminescence from silicon-vacancy (Si-V) defect centers. The precision-patterned pre-growth seeding of nanodiamonds is achieved by scanning probe “Dip-Pen” nanolithography technique using electrostatically-driven transfer of nanodiamonds from “inked” cantilevers to a UV-treated hydrophilic SiO₂ substrate. The enhanced emission from nanodiamond-dots in the far-red is achieved by incorporating Si-V defect centers in subsequent chemical vapor deposition treatment. The development of a suitable nanodiamond ink, mechanism of ink transport, and effect of humidity, dwell time on nanodiamond patterning are investigated. The precision-patterning of as-printed (pre-CVD) arrays with dot diameter and dot height as small as 735 nm ± 27 nm, 61 nm ± 3 nm, respectively and CVD-treated fluorescent ND-arrays with consistently patterned dots having diameter and height as small as 820 nm ± 20 nm, 245 nm ± 23 nm, respectively using 1 s dwell time and 30% RH is successfully achieved. We anticipate that the far-red intense photostable luminescence (~738 nm) observed from Si-V defect centers integrated in spatially arranged nanodiamonds could be beneficial for the development of the next generation fluorescent based devices and applications.

Keywords

Fluorescent NanoDiamond (FND); scanning probe “Dip-Pen” nanolithography; Raman mapping; atomic force microscopy; room temperature photoluminescence

1. Introduction

Nanodiamonds (NDs) offer an emergent technology with one of its main applications as a perfectly photostable luminescent emitter upon incorporation of defect centers in combination with the notable properties such as biocompatibility [1, 2], non-toxicity [3, 4], rich surface chemistry and easy surface functionalization with a wide range of therapeutics [5]. The characteristic zero-phonon line emission from ND is only dependent on the type of

defect present, and therefore some degree of ND particle size distribution is still able to maintain the characteristic emission. While nitrogen-vacancy (NV) centers are widely studied in ND for quantum optical and biological imaging applications [6, 7], the silicon vacancy (Si-V) defect center has emerged as an alternative emitter because of its numerous promising properties. Since the silicon atom enters the diamond lattice interstitially and sits at the center of a split vacancy, this center does not couple strongly with diamond phonons (in contrast to NV center) [8]. The result is a brighter and narrower zero-phonon line emission from the Si-V center at ~738 nm (FWHM ranging from 0.7 to ~10 nm). It has relatively weak phonon coupling [9, 10] that is distinct from the characteristic broad band photoluminescence of ND (spread between 450 nm and 650 nm) [11, 12]. Emission from the Si-V center is also readily observed even for weakly agglomerated sub-10 nm size diamond [9, 13], in contrast to the NV center which is known to have low probability for incorporation in sub-10 nm particles [14–16]. The zero-phonon lines associated to both charge states of NV (i.e. 575 nm for NV⁰ and 638 nm for NV⁻) are typically overshadowed in intensity by a superimposed broad phonon side band (~100 nm) due to strong electron-phonon coupling [11], which may limit spectral distinction between the desired defect center fluorescence and that from background autofluorescence in a biological environment [17]. These aspects, combined with the recently observed enhancement in Si-V luminescence associated with nitrogen-doping [18] makes the Si-V center worthy of further study. The Si-V center has been investigated mainly in the form of thin chemical vapor deposited (CVD) films with less consideration in the form of isolated nanocrystals, which are particularly relevant as biolabels or as a drug-delivery platform. Furthermore, the development of future nanoscale devices that harness the remarkable luminescent properties of NDs will require exceptional spatial control. Micro/nano patterning of diamond can be achieved by either direct etching of post-growth diamond CVD films or pre-growth selective seeding. The post-growth patterning of diamond involves expensive direct etching techniques such as ion beams, lasers etc. [19, 20]. On the other hand, the pre-growth selective deposition involves various crucial processing steps such as patterning of mask materials [21] and etching [22].

To this end, we report a combined novel approach to fabricate spatially controlled fluorescent ND-array based on the pre-growth precision-patterned seeding of NDs by using the scanning probe “Dip Pen” Nanolithography (DPN) technique with subsequent CVD treatment to incorporate Si-V defect centers. In this way, we can achieve high resolution precision-patterned fluorescent ND-arrays that contain perfectly photostable far-red luminescence based on Si-V defect centers. DPN has been utilized to write compositions containing nanomaterials and polymers [23]. However, this article is the first report of ND patterning using the DPN approach with CVD-induced fluorescence of DPN ND-arrays to our knowledge. Stable ND-arrays were achieved by taking advantage of electrostatically-driven transfer of ND-based “inks” to UV-treated SiO₂ substrates. The effect of humidity and dwell time on patterning was investigated. The results observed in this study could have exciting implications in fluorescent based controlled-release of therapeutics or sensitive biosensing.

2. Experimental Details

2.1 Preparation of stable ND-ink

For effective tip to substrate transfer of ND using the DPN technique, an “ink” consisting of the ND particles in a polymeric carrier solution was developed. Several critical factors regarding ink development such as dispersion of NDs in the ink, its stability within the tip/substrate meniscus during printing, ink viscosity, and chemical affinity between ink and substrate must be considered. We found that water or organic solvent-based ND-inks were not effective in printing NDs with consistency or high spatial resolution. Higher viscosity glycerol-based ND inks also were not sufficient to allow effective transfer from tip/

substrate, with much of the ink remaining on the tip during printing. Instead, we relied on electrostatic interactions between positively charged amino groups of linear-polyethylenimine (PEI) and NDs having surface functional groups (i.e. carboxyl and hydroxyl groups) of primarily negative charge (as shown in Figure 1A), along with SiO₂ substrates prepared to have negative charge. PEI behaves like a positively charged polyelectrolyte in an aqueous solution with pH<9 because of a relatively high density of positively charged amino groups (as shown in Figure 1A) and is electrostatically attracted onto negatively charged SiO₂ [24].

The ND-based ink including dimethyl sulfoxide (DMSO), PEI and glycerol was developed for optimal printing as shown in Figure 1B. DMSO was chosen to improve solubility and printing ability as it evaporates sufficiently slowly to allow time for ND transport to the surface. Synthetic high-temperature/high-pressure diamond (Engis Corp.) with an average particle size distribution ranging from 40 nm to 60 nm was used as raw material. ND-ink preparation was a 3-step process as shown in Figure 1B. First, very stable ND slurry (2% w/v) was prepared by dispersing as-received NDs in DMSO (MP Biomedicals LLC.) and ultrasonicated for 60 min. In parallel, 0.4% of linear polyethylenimine (PEI) (MW~25,000; Polyscience Inc.) was dissolved in DMSO and sonicated for 60 min. Second, the ND slurry (in DMSO) was added to PEI (in DMSO) followed by 30 min sonication and overnight medium stirring to achieve coating of ND with PEI (pH =8). Finally, 40% glycerol (99+%, Alfa Aesar) was added into the ink prepared in the second step followed by 60 min stirring. Glycerol was added to modify ink wettability at the tip/substrate as well as to increase the viscosity of the ink for improved feature resolution and printing consistency. The viscosity of the ink was estimated by using a Brookfield DVII+Pro cone/plate viscometer. At 25.5 °C, the measured viscosity of the base polymeric carrier solution (PEI+DMSO+Glycerol) was 14.01±0.04 cp and that of the final PEI+DMSO+Glycerol+ND ink was 16.87±0.01 cp.

2.2 Precision-Patterning of ND-array using Dip-Pen nanolithography

ND precision-patterning by DPN onto SiO₂ substrate was investigated for a range of relative humidity (RH) and dwell times (DT), factors known to influence feature resolution of DPN-printed liquid inks [25, 26]. Silicon substrates with a thermally grown oxide layer (300 nm) and lithographically patterned fiducial marks was obtained from Nanoink Inc. The SiO₂ substrates were ultrasonically cleaned successively with acetone, ethanol, and deionized water for 10 min each. To promote the formation of a water meniscus between the cantilever and substrate as well as to increase the electrostatic interaction of amino groups of positively charged PEI+ND with the SiO₂ substrate, the SiO₂ was rendered hydrophilic by UV-ozone treatment (using UV-ozone cleaner; Model 42, Jelight Company Inc.) for ~2 min. Room temperature static water contact angle was measured by ThetaLite 101 tensiometer (Biolin Scientific). The static water contact angle decreased from 45° to 3–5° before and after UV-ozone treatment, respectively. ND-ink patterning into dot arrays was achieved using type-M, “A-framed” Si₃N₄ AFM probes (Nanoink Inc.) with high stiffness and spring constant (0.6 N/m, Pitch=66 μm). A-framed AFM probes have a recessed area surrounding the tip to increase loading of ink material and extend printing time. The tips were coated by directly dipping them into the as-prepared ND-ink and brought into contact with SiO₂ surface using a constant height contact lithography mode as shown in Figure 1B. A water meniscus naturally forms between the ink-coated tip and the SiO₂ substrate under ambient conditions. Provided a sufficient driving force exists for transfer of ink to the substrate, capillary transport through the meniscus will occur. As expected from its cationic character, ND+PEI-based ink effectively transferred to the hydrophilic SiO₂ surface, presumably due to electrostatic interactions between the hydrophilic SiO₂ and PEI. Figure 1B illustrates schematically how the negatively charged surface of NDs was anchored onto the UV-Ozone treated SiO₂ surface via cationic PEI electrostatic interaction. ND-arrays of 66×66 μm² were

precisely patterned onto SiO₂. Patterned arrays were created using 30%, 50%, and 70% relative humidity with dot separation of 11 μm and 22 μm and dwell time ranging from 1 sec to 7 sec. Relative humidity was adjusted within the enclosed patterning chamber via a distilled water bubbler/dry nitrogen diffuser feedback system. All patterning experiments described herein were conducted at 23 °C. Close-contact mode AFM 3-D topographical image of a ND-array patterned with 11 μm spacing, 1 sec dwell time and 30% RH shows dot elements with consistent average height (61 ± 3 nm) and separation as depicted in Figure 1C.

2.3 Incorporation of Si-V defect centers in ND dots using microwave plasma chemical vapor deposition

In a subsequent processing step to incorporate Si-V defects luminescent centers in as-printed ND dots by DPN, we used microwave plasma chemical vapor deposition (MPCVD). Samples containing as-printed ND-array were placed in the CVD chamber and treated in hydrogen rich plasma with 0.7% CH₄, and 0.04% N₂, 45 Torr operating pressure, 900 W microwave power, and 820 °C substrate temperature for 30 min [18]. Incorporation of Si-V defects occurs as a result of plasma chemical etching of the exposed Si substrate (also quartz components of a microwave chamber) by the atomic hydrogen in the hydrogen-rich plasma. The main source of silicon in the formation of Si-V defect center is the SiO₂ substrate. The etched gasified silicon species are re-deposited along with newly-formed diamond onto the existing ND array to form the defect center [9]. The increase in dot size after CVD treatment is due to the additional diamond deposited on each dot, along with incorporated Si-V centers. The effect of CVD treatment on ND dot size is shown in Figure 7 and discussed in later section 3.5.

3. Results and Discussion

3.1 Analysis of ND-ink using Dynamic Light Scattering

Dynamic light scattering measurements (Zetasizer Nano ZS; 3000HS, Malvern Instruments, Ltd.) were performed to determine the size distribution and zeta-potential (ζ) of PEI, ND, and ND+PEI. As-received NDs dispersed in DMSO have a left-skewed size distribution (number density) with peak at 61 nm (band width ± 17 nm) and mean size distribution of 86 nm. After PEI addition, the ND+PEI particle size distribution (number density) peaked at 58 nm (band width ± 18 nm) with mean size increased to 96 nm. A largely negative zeta-potential of -28.6 mV measured for the as-received NDs dispersed in DMSO was attributed to the presence of ionized carboxyl groups ($-\text{COO}^-$) and hydroxyl ($-\text{OH}$) functional groups on ND surface at pH=8 (Figure 1A). After PEI addition the zeta-potential shifts from negative to a positive value of $+25.2$ mV due to the positively charged secondary amines present in Linear-PEI (Figure 1A). For reference, the zeta-potential of NDs before and after PEI addition was measured to be -63.8 mV and $+43.4$ mV, respectively, when dispersed only in deionized water. No significant precipitation or agglomeration was observed after PEI addition suggesting that cationic PEI is coated on individual and/or very small aggregates of NDs as illustrated schematically in Figure 1B. The negative electrostatic potential of NDs ensured high dispersion stability and attachment to the cationic PEI.

3.2 Analysis of ND-ink using Fourier Transform Infrared Spectroscopy

Different ink formulations i.e. PEI+DMSO, ND+DMSO, and PEI+DMSO+ND were dropped onto KBr pellet to perform Fourier Transform Infrared Spectroscopy (FTIR) experiments in standard transmission by using Nicolet™ FT-IR spectrometer (Thermo Electron Corporation). FTIR spectra of as-received ND, PEI, and ND+PEI are shown in Figure 2. FTIR spectrum of neat DMSO onto KBr was subtracted from each of ink formulations i.e. PEI+DMSO, ND+DMSO, and PEI+ND+DMSO to get PEI, ND, and PEI

+ND spectra. Carboxylation of the ND surface was verified by well-resolved bands of C=O and O-H stretching of carboxyl functional groups near 1700–1865 cm^{-1} and 3050–3650 cm^{-1} (shown in inset), respectively. The broad band extended between 3050–3650 cm^{-1} (shown in inset) is associated with an amine N-H stretch in PEI. The O-H contribution in the range 3050–3650 cm^{-1} could be attributed to adsorbed water in addition to ND functional groups and PEI amine groups. The observed decrease in the intensity of broad band in 3050–3650 cm^{-1} region for the ND+PEI mixture indicates that the O-H functional groups of as-received ND are replaced by N-H groups of PEI. This supports the claim that the positively charged PEI was electrostatically adsorbed onto the surface of negatively charged NDs, covering the particles with amine groups of PEI. The peaks at $\sim 1460 \text{ cm}^{-1}$ and $\sim 1605 \text{ cm}^{-1}$ are assigned to amide CH_2 and amine N-H bending of PEI respectively, as indicated with dotted lines in Figure 2. The region between 1530–1700 cm^{-1} consists of two well-separated peaks at 1660 cm^{-1} (C=C stretch) and 1605 cm^{-1} (for PEI) and 1646 cm^{-1} and 1605 cm^{-1} (for ND+PEI). For as-received ND, a broad O-H bending band at 1634 cm^{-1} with a weak shoulder at 1656 cm^{-1} is attributed to a C=O stretch from carboxylic surface groups on the ND surface. For ND+PEI, a peak shift is particularly evident in the region 1520–1260 cm^{-1} where the peak related to C=C at 1403 cm^{-1} moves to 1380 cm^{-1} . The three peaks at 1203 cm^{-1} , 1127 cm^{-1} , and 1100 cm^{-1} can be assigned to C-O and/or C-N groups.

3.3 Characterization of Precision-Patterned ND-array using Micro-Raman spectroscopy and Raman Mapping

Micro-Raman spectroscopy was performed in order to verify the presence of diamond within each dot for both as-printed and CVD-treated using Nd: YAG solid state laser source with 532 nm excitation power and laser spot size $\sim 4 \mu\text{m}^2$ focusing on individual dots within the ND-array as shown in Figure 3(a) and 3(b). In the Raman spectrum of as-received NDs shown in Figure 3a (i), the sharp peak at 1332 cm^{-1} indicates crystalline diamond and the broad band between 1580 cm^{-1} to 1590 cm^{-1} (G-band) is associated with disordered sp^2 carbon. Figure 3a (ii) and 3b (iii) show Raman spectra from two representative as-printed dots to reveal the range in structure between several measurements of as-printed ND dots. The peak at 1464 cm^{-1} as well as high background from 1050 cm^{-1} to 1420 cm^{-1} with broad peaks at 1060 cm^{-1} , 1109 cm^{-1} and 1265 cm^{-1} are attributed to glycerol [27]. The broad “D” and “G” bands at 1350 cm^{-1} and 1590 cm^{-1} , respectively, in Figure 3a (ii) are associated with disordered graphitic carbon. However, the broad “D” band can mask an underlying crystalline diamond peak, and both 3a (i) and 3a (ii) spectra are representative of varying quality grades of nanostructured diamond. After CVD treatment the intensity of the diamond Raman signal at 1332 cm^{-1} increased due to CVD-deposited diamond on the ND seed. This is shown in Figure 3b (i–iv) for four separate diamond dots and is meant to convey the range of post-CVD structures observed. Some dots show peaks at 1128 cm^{-1} and/or 1480 cm^{-1} which have been associated with trans-polyacetylene, often observed in the growth of CVD ND [28]. The observed variation in the Raman signal from the as-printed as well as CVD-treated ND-array could be attributed to the variation in the structure, phase purity, sp^3/sp^2 ratio, crystal size and surface functional groups in the as received NDs. We anticipate that further purification of as-received ND as well as post-patterned annealing in inert gas to order to remove non-diamond components will minimize this variation.

Micro-Raman System (Horiba Jobin Yvon, LabRam HR 800 UV) equipped with 800 mm focal length spectrometer optimized for 200–1600 nm spectral region, 600 g/mm grating with an excitation light source He-Ne laser 632.8 nm and $\sim 2 \text{ mW}$ incident power at the sample was used for Raman mapping to examine spatial distribution of ND dot array and diamond structure. Figure 3(c) shows an optical image of a CVD-treated ND array printed at 30% RH and 1 s dwell time with 11 μm dot spacing. The Raman-mapped area is indicated

by the red square enclosing four dots in Figure 3(d). Crystalline diamond is shown mapped in a narrow spectral region centered around 1332 cm^{-1} and appears blue in the mapping while the surrounding red color is associated with a spectral range centered around 920 cm^{-1} due to the substrate. Figure 3(e) shows corresponding Raman spectra from the four dots as well as from a location between the dots on the SiO_2 surface. It should be noted that sp^2 -bonded carbon will be absorbed more at 632 nm laser excitation compared to 532 nm excitation and therefore the non-diamond spectral components are of higher intensity here compared to the Raman spectra taken at 532 nm (Figure 3b) [29]. In addition, the Raman scattering cross-section of graphitic carbon is about 50 times that of diamond. Given the higher Raman sensitivity of non-diamond carbon phases, especially for higher excitation wavelengths, the data in Figure 3(b & e) suggest that the majority of material remaining in the precisely-patterned post-CVD treated arrays is sp^3 -bonded carbon. In addition no carbon-related structures were detected in between the dots.

3.4 Characterization of Precision-Patterned ND-array using Fluorescence Microscopy and Room Temperature Photoluminescence

Room temperature photoluminescence spectroscopy and fluorescence microscopy were used to investigate the luminescence properties of ND dots within the patterned ND-arrays. A Zeiss Axio Imager A2 fluorescent microscope (with X-cite series 120Q light source) was used for epi-fluorescence imaging with three different excitation and emission filter-sets. The corresponding filter cubes used excitation band pass, dichroic, and emission band pass sets, respectively, as follows (Green: $470\pm 20\text{ nm}$, 495 nm , $525\pm 25\text{ nm}$), (Yellow-Red: $494\pm 10\text{ nm}$, 570 nm , $605\pm 35\text{ nm}$), and (Far Red: $550\pm 13\text{ nm}$, 695 nm , $725\pm 25\text{ nm}$). Pseudo-colored epi-fluorescence images of (a) randomly dispersed as-received NDs, (b) as-printed ND-array, (c) CVD-treated ND-array for small dots, and (d) CVD-treated ND-array for relatively large dots are presented in three different spectral regions are shown in Figure 4. The green fluorescence ($500\text{--}550\text{ nm}$), yellow-red fluorescence ($570\text{--}640\text{ nm}$) and far-red fluorescence ($700\text{--}750\text{ nm}$) are shown in first, second, and third row of Figure 4. As-received and DPN-patterned ND-array show strong green fluorescence in the spectral range $500\text{--}550\text{ nm}$, often a result of naturally occurring H3 centers (N-V-N defect with emission maximum near 530 nm) as well as yellow-red fluorescence in the range $570\text{--}640\text{ nm}$ that could be due to the broad emission tail of this intrinsic defect in addition to other nitrogen related defects [30]. The fluorescence in the $700\text{--}750\text{ nm}$ spectral range where the Si-V zero phonon line at 738 nm (accompanied by a weak phonon side band) is expected to emit was not easily detectable for both as-received and pre-CVD patterned ND arrays. This is illustrated in the 3rd row of column 4(a) and 4(b). However, after CVD treatment intense far-red fluorescence related to the Si-V center was readily detected. As a result of CVD treatment, this far-red fluorescence intensity increased by a factor of 5.7 (average gray scale 8-bit pixel value) for the small dot ND array and by a factor of 3.7 for the larger dot ND array as shown in 3rd row of Figure 4 (c) and 4 (d). Our preliminary data has already demonstrated the feasibility of modifying as-received ND to achieve intense far-red fluorescence from Si-V centers, along with further enhancement of this fluorescence using nitrogen doping [18]. The variation in size of patterned dots as seen in Figure 4 (c) and 4 (d) is a result of different amounts of ink coated onto the cantilever tip. If the tips are coated uniformly with a comparatively less amount of ink, smaller dots are produced. If the tips are coated with copious amounts of ink, larger dots will be created at the same relative humidity and dwell time because of a larger meniscus that forms.

Room temperature photoluminescence spectroscopy (excitation wavelength at $\sim 532\text{ nm}$, Nd:YAG solid state laser source) was performed on different ink components as well as on as-printed and CVD treated ND-arrays. The room temperature photoluminescence spectra for as-received ND, as-printed (PEI+DMSO+Glycerol) control dot, as-printed (PEI+DMSO

+Glycerol+ND) dot, and CVD-treated (PEI+DMSO+Glycerol+ND) dot are shown in Figure 5. As-received NDs have very broad strong luminescence that is peaked at ~650 nm. The room temperature photoluminescence from polymeric ink (PEI+DMSO+Glycerol) control dots shows a very broad luminescence peaked at ~583 nm. The fluorescence from the polymeric matrix is quite strong and extended up to ~680 nm. However, it can be carefully observed that luminescence intensity from (PEI+DMSO+Glycerol) polymeric control dots around ~650 nm is very weak where, a broad luminescence peak at ~650 nm from as-received NDs is detected. When NDs were added into the PEI+DMSO+Glycerol, broad luminescence signal is shifted to the red region and it can be noticed that luminescence intensity around 650 nm from (PEI+DMSO+Glycerol+ND) as-printed dots is also increased compared to the PEI+DMSO+Glycerol polymeric dot luminescence. An observed red-shift of ~34 nm for as-printed DPN dots after ND addition into the polymeric ink formulation could be ascribed to the broad fluorescence of as-received NDs extended from 565–740 nm. The broad luminescence signal from as-printed (PEI+DMSO+Glycerol+ND) dot can be observed as a combination of two broad luminescence signals, one peaked at ~583 nm because of the PEI +DMSO+Glycerol polymeric content overlapped with second signal from the ND around 650 nm. After CVD treatment all the polymeric contents i.e. PEI+DMSO+Glycerol have been removed and luminescence signal is similar to the as-received ND spectrum except the fact that now there is an intense peak at ~738 nm associated to Si-V defect center. While pre-CVD patterned dot array show strong green-yellow fluorescence, far-red fluorescence due to Si-V defects centers with emission maximum at 738 nm (FWHM ~7 nm) can only be readily detected in patterned ND dots treated by CVD.

3.5 Characterization of Precision-Patterned ND-array using Close-Contact Mode AFM

Atomic force microscopy (DPN5000, Nanoink Inc.) in close-contact mode was used to evaluate dot diameter and height, scalability of the ND-array as well as size consistency using plots of dwell time vs. dot size. The effect of relative humidity on dot size for each dwell time is shown Figure 6 for as-printed ND dots. Dot diameter and height were measured for dwell times ranging from 1 to 7 s. For a given dwell time both the dot diameter and height increase linearly (linear fit with $R^2 = 0.97$ to 0.99) with respect to relative humidity as shown in Figure 6(a) and 6(b). Printing at higher relative humidity (e.g. 70%) resulted in a larger spread in dot size with dwell time. A higher humidity increases the size of the condensed meniscus between the tip and the surface, resulting in more lateral ink spreading and larger printed dots. Both the height and diameter of as-printed ND dots increase roughly by factor of 2–3 time, depending on relative humidity and dwell time. More detailed estimation of increase in as-printed ND-dot diameter and height; depending on relative humidity and dwell time is given in Table-1 and Table-2 of supplementary data, respectively. Again, CVD-treated dots are larger since additional ND material is deposited on the dot array during incorporation of Si-V defects in this process. From pre- to post-CVD, dot diameter and height increased by roughly factors of 1–3 and 4–5 times, respectively, depending on relative humidity and dwell time. Figure 7(a) and 7(b) show a linear dependence (linear fit $R^2 = 0.97$ to 0.99) of dot diameter and dot height respectively with the square root of dwell time. As-printed (pre-CVD) arrays can be consistently printed with dot diameter as small as $735 \text{ nm} \pm 27 \text{ nm}$ and dot height as small as $61 \text{ nm} \pm 3 \text{ nm}$. We have achieved CVD-treated ND arrays with consistently patterned dots having diameter as small as $820 \text{ nm} \pm 20 \text{ nm}$ and dot height as small as $245 \text{ nm} \pm 23 \text{ nm}$ using 1 s dwell time and 30% RH. More detailed estimation of increase in ND-dot height and diameter after CVD treatment at relative humidity 30% for each dwell time is given in Table-3 and Table-4 of supplementary data, respectively. The effect of dwell time on the DPN feature size is ambiguous in literature. For molecular inks the deposition rate is dependent on the diffusion rate of the molecule, which is different for each molecule. Thus, the size of the DPN feature is controlled by the tip/surface dwell-time and the size of the water meniscus, which is

determined by the humidity conditions. A dependence of feature size on the square root of the dwell time had been reported for various molecular inks [25, 31, 32]. However there are some other descriptions where the DPN feature size increased initially with respect to dwell time and saturates for higher dwell times [33]. On the other hand deposition properties of liquid-inks are determined by the interactions between the liquid-ink and the tip, the liquid-ink and the surface, and viscosity of the liquid-ink. These interactions limit the minimum feature size of the liquid ink to about $>1\ \mu\text{m}$. A dependence similar to molecular ink where the DPN feature size increases initially with respect to dwell time and saturates for higher dwell times was also observed for PbTiO_3 [34], silver nanoparticles [35] based ink. A rather quadratic trend was reported for biologically active protein nano-arrays [36]. No correlation was observed between tip dwell times and Gold nanoparticle deposition for times ranging from 20 sec to 120 sec [37]. In our study we observed The ND dot size has a strong linear dependence on the square root of dwell time which is similar to the molecular where the dot size exhibits the expected $t^{1/2}$ dependence [25, 31, 32].

4. Conclusions

A new method for pre-CVD-growth precision patterned seeding of nanodiamonds in form of dot-array onto SiO_2 was demonstrated using scanning probe “Dip-Pen” Nanolithography (DPN) technique. The incorporation of photostable Si-V luminescent centers with enhanced far-red fluorescence (c.a. 738 nm) into individual dots in the ND-array was performed by subsequent CVD treatment of the as-printed ND-array. Effective precision patterning of ND features in terms of achieving efficient tip-substrate ink transfer, dot consistency, and resolution was achieved using an ND-ink mixture based on PEI+DMSO+Glycerol matrix having electrostatic interactions as a driving force for maintaining ink stability and affinity to UV-ozone treated hydrophilic SiO_2 substrates. The dot size in as-printed and CVD-treated ND arrays was strongly influenced by both relative humidity (RH) and dwell time, with the smallest CVD-treated stable dots $820\ \text{nm} \pm 20\ \text{nm}$ diameter, $245\ \text{nm} \pm 23\ \text{nm}$ height prepared at the lowest RH and dwell time (30% and 1 s, respectively). Although Raman spectroscopy confirmed the presence of diamond within each patterned dot, the polymeric carrier ink composition and the post-patterned CVD treatment resulted in significant variation in sp^2/sp^3 carbon bonding. Nevertheless, the post-patterned CVD treatment created spatially-registered Si-V defect centers within each ND dot, yielding bright far-red emission (c.a. 738 nm with FWHM $\sim 7\ \text{nm}$) which is otherwise not present in the pre-CVD as-patterned ND-array. Fluorescence from Si-V defects in ND may be particularly useful for fluorescent based biomedical applications due to its extreme photostability and narrow-band emission that is well-separated from endogenous auto-fluorescence. Precision patterning of nanodiamonds may lead to the next-generation of easily-standardized devices with high-fidelity enhanced sensing, imaging, and drug-delivery capability.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

(A) simplified schematic of as-received ND surface showing the presence of carboxyl (-COOH) and hydroxyl (-OH) functional groups that makes ND surface negatively charged with zeta-potential of -28.6 mV when dispersed in DMSO and structure of linear PEI (L-PEI) (Mw=25,000). (B) A simplified illustration of basic ND-ink preparation and DPN writing is presented here. Very stable slurry prepared by dispersing as-received NDs in DMSO is added to the L-PEI dissolved in DMSO. Negatively-charged surface of ND electrostatically interacts with secondary amines of L-PEI. AFM tip is dip coated with ND-ink based (ND+PEI+DMSO+Glycerol) and patterned onto UV-ozone treated hydrophilic SiO₂ substrate. The positively-charged surface of PEI coated ND is electrostatically adsorbed onto hydrophilic SiO₂. (C) Non-contact mode AFM 3-D topographical image of a ND-array using "ND-ink" (PEI+ND+DMSO+Glycerol) on UV-Ozone treated SiO₂ surface patterned by DPN at RH=30% and DT=1 sec. The dots in ND-array demonstrate uniformity of feature size.

Figure 2.

FT-IR absorption spectra of ND, PEI, and ND+PEI are showing the presence of a broad band extended from 1700–1865 cm^{-1} related to carboxylic acid C=O stretch, amine N-H bending at 1605 cm^{-1} and amide CH_2 peak at 1460 cm^{-1} . Inset shows the O–H contribution in the range 3050–3650 cm^{-1} that could be attributed to adsorbed water in addition to ND functional groups and PEI amine groups.

Figure 3.

(a) Raman spectra (excitation at ~ 532 nm) of as-printed ND array showing (i) as-received NDs and (ii), (iii) two representative as-printed DPN ND dots (b) Raman spectra of CVD-treated ND dots showing four representative spectra from post-CVD dots (i), (ii), (iii) and (iv) (c) Optical microscopy image of the 2D mapping area of the ND array created by DPN after CVD treatment (d) 2D Raman intensity mapping, and (e) Raman spectra of four dots and background using excitation at ~ 632 nm.

Figure 4. Pseudo-colored epi-fluorescence images (scale bar:20 μ m) of (a) as-received NDs, (b) as-printed ND-array, (c) CVD treated ND-array for small dots, and (d) CVD treated ND-array for big dots. Three different emission ranges namely 500–550 nm, 540–670 nm, and 700–750 nm are shown in the first, second, and third row of each column, respectively. After CVD treatment ND-array shows readily observable far-red luminescence because of Si-V defect center incorporation as shown the 3rd row of column (c) and (d).

Figure 5.

The room temperature photoluminescence spectra (excitation at ~532 nm) shows a red-shift from ~583 nm to ~617 nm after ND addition in PEI+DMSO+Glycerol polymeric ink carrier. The broad luminescence signal from as-printed dot of PEI+DMSO+Glycerol+ND can be observed as a combination of two broad luminescence signals, one peaked at ~583 nm because of the PEI+DMSO+Glycerol polymeric content overlapped with second signal from the ND peaked around ~650 nm. After CVD treatment all the polymeric contents i.e. PEI +DMSO+Glycerol have been removed and luminescence signal is similar to the as-received ND spectrum in addition to an intense peak at ~738 nm (FWHM ~7 nm) associated to Si-V defect center.

Figure 6.

Close-contact mode AFM topographic images (scale bar: 1 μm) showing the effect of relative humidity on as-printed DPN ND dot size for each dwell time ranging from 1 sec to 7 sec.

Figure (a) and (b) present as-printed ND dot diameter vs. relative humidity, and dot height vs. relative humidity respectively. The error bars represent standard deviation of four dots.

Figure 7.

Close-contact mode AFM topographic images (Scale bar: 1 μm) of as-printed and CVD treated DPN ND-array for dwell time 1 to 7 sec created at 30% RH. Figure (a) and (b) show the effect of CVD treatment on dot diameter, and dot height respectively. The error bars represent standard deviation of four dots shown in the close-contact mode AFM images.