Surface modification and stability of detonation nanodiamonds in microwave gas discharge plasma

Andrei V. Stanishevsky*, Michael J. Walock, Shane A. Catledge

Department of Physics, University of Alabama at Birmingham, Birmingham, AL 35294, USA.

Abstract

Detonation nanodiamonds (DND), with low hydrogen content, were exposed to microwave plasma generated in pure H₂, N₂, and O₂ gases and their mixtures, and investigated using X-ray diffraction (XRD), Fourier Transform Infrared (FTIR), Raman, and X-ray photoelectron spectroscopies. Considerable alteration of the DND surface was observed under the plasma conditions for all used gases, but the diamond structure of the DND particle core was preserved in most cases. The stabilizing effect of H₂ in H₂/N₂ and H₂/O₂ binary gas plasmas on the DND structure and the temperature-dependent formation of various CNH_x surface groups in N₂ and H₂/N₂ plasmas were observed and discussed for the first time. DND surface oxidation and etching were the main effects of O₂ plasma, whereas the N₂ plasma led to DND surfaces rich in amide groups below 1073 K and nitrile groups at higher temperatures. Noticeable graphitization of the DND core structure was detected only in N₂ plasma when the substrate temperature was above 1103 K.

Keywords: nanodiamond; microwave; plasma, modification; surface; spectroscopy

* Corresponding author. Tel.: +1 205 934 8030; fax: +1 205 934 8042
E-mail address: astan@uab.edu

1. Introduction

Crystalline diamond nanoparticles prepared by detonation techniques [1] maintain most of the physical properties of bulk diamond and exhibit a rich surface chemistry that makes this material very attractive for a large variety of applications ranging from polishing pastes [2] and fillers in polymer-based composites [3,4] to drug carriers [5,6] and bio-markers [7]. Many of these applications require additional modification of the commercial detonation nanodiamonds (DND) to reduce the agglomerate size and obtain colloids of primary nanocrystals, or to optimize the DND particle surface chemistry for specific purposes [8-10].

Among the different techniques used to modify DND particles, gas discharge plasma treatment has been demonstrated to be an effective tool for the chemical modification of DND surfaces. Several different gases (H_2 , O_2 , CF_4 , SF_6 , N_2) and plasma generation techniques have been used to de-agglomerate DND particles and improve their dispersibility in water [11,12], change wettability [13] and electric conductivity [14], and introduce new surface functionality [15,16]. For example, Gibson et al [12] exposed DND to atmospheric-pressure glow discharge plasma in O_2 and N_2 gases for different period of times. They found that plasma treatment reduced the size of DND particles. It was also noted that N_2 plasma was more efficient than O_2 plasma in de-agglomerating DND particles, and short treatment times produced smaller sized particles than longer treatment times. However, the changes in chemical composition of those plasma-treated DND particles were not examined. Kozak et al [17] noted a significant increase in the amount of surface C=O groups and disappearance of C-H groups after O_2 radio-frequency discharge plasma treatment of 5-nm DND particles. The opposite effect was observed by Liu et al [18] when hydrogen plasma was used. Arnault et al [19] determined that substrate temperature plays an important role during DND hydrogenation in H_2 microwave plasma. It was shown that

if the substrate temperature was 793 K, C-O bonds could not transform into C-H bonds. During a 15-minute plasma processing time, the amount of oxygen species in DND gradually reduced as temperature increased from 793 K to 973 K, and all oxygen was removed during that time interval at 973 K. The same group also found that DND particles, when used as a seed layer for growing diamond films in a chemical vapor deposition (CVD) process, exhibit remarkable stability during hydrogen microwave plasma treatment at substrate temperatures of up to 1213 K [20].

The goal of present work was to further the understanding of microwave gas discharge plasma interaction with DND particles. Surface modification of DND in N_2 , H_2/N_2 , and H_2/O_2 gas plasma was studied from the standpoint of achieving better control of surface chemistry and providing DND particles with new functionalities, when compared with only hydrogen or oxygen plasma. Temperature-dependent formation of amide and nitrile groups and a stabilizing effect of H_2 on DND structure and surface chemistry in H_2/N_2 and H_2/O_2 gas mixtures were observed for the first time. X-Ray Diffraction (XRD), Fourier Transform Infrared (FTIR), Raman, and X-ray Photoelectron Spectroscopy (XPS) were used to analyze and explain the chemical and structural changes in DND samples after the plasma processing.

2. Experiment

Detonation nanodiamond powders (SINTA Joint-Stock Co, Minsk, Belarus) with a primary crystallite size of 6 ± 1 nm and specific surface area of $295\text{ m}^2/\text{g}$, according to the material specifications, were ultrasonically dispersed in de-ionized water, then precipitated in equal amounts (0.75 mg) onto $7\times 7\text{ mm}^2$ intrinsic silicon substrates ($480\text{ }\mu\text{m}$ thickness) and dried in air at 343 K. Silicon substrate was selected due to its stability in microwave plasma and sufficient

transparency in infrared region of interest. After drying, 70 ± 30 μm -thick porous layers of aggregated DND particles were formed. The samples were placed in a 6 kW 2.4 GHz Wavemat Microwave Plasma Chemical Vapor Deposition (MWCVD) reactor, and exposed to microwave gas plasmas at 600 W average power for 45 minutes. In case of individual gas plasmas, the processes were run in H_2 (20 Torr or 27 Torr chamber pressure depending on the process, 500 sccm flow rate, substrate temperature self-ramped to 923 ± 40 K or to 1013 ± 40 K), O_2 (15 Torr / 10 sccm flow, substrate temperature self-ramped to 703 ± 15 K) and N_2 (15 Torr / 36 sccm, substrate temperature self-ramped up to 1048 ± 25 K or to 1128 ± 25 K). During the plasma treatment in O_2 , and N_2 , hydrogen gas was initially used for 5 minutes to stabilize the plasma and heat the substrate. In case of gas mixtures, the following process parameters were used: H_2/O_2 mixture (20 Torr pressure, flow rate 12 sccm and 10 sccm, respectively, substrate temperature self-ramped to 1033 ± 25 K) and H_2/N_2 mixtures (27 Torr total pressure, flow rate 10 sccm and 36 sccm, respectively, substrate temperature self-ramped to 1128 ± 25 K). The substrate temperature was monitored throughout the process by a two-color Mikron L77LS optical pyrometer. After the process, the samples were cooled down in a low-pressure hydrogen atmosphere.

FTIR spectra (Vertex 70 spectrometer, Bruker Optics) were acquired in transmission mode directly from DND samples on intrinsic silicon substrate, and the substrate background spectra were subtracted. In all cases, the FTIR spectra represented an average of 100 scans recorded with a resolution of 4 cm^{-1} for each sample.

Philips X'pert MPD thin-film X-ray diffractometer with a $\text{Cu K}\alpha$ tube ($\lambda = 0.15406\text{ nm}$) operating at 45 kV and 40 mA was used to determine the crystalline phase composition. The detector was scanned between 20° and 70° , with a constant take off angle of 5° . Mean crystal size

was determined using the Lorentzian fitting of diamond (111) peak in the XRD spectrum and Scherrer equation.

Raman microspectroscopy was employed at 532 nm and 325 nm excitation wavelengths to determine any plasma-induced peculiarities in DND samples. Raman spectra were collected from several locations across each sample using a Dilor XY system equipped with a 300 mW solid state laser (Dragon Lasers, China), operating at $\lambda=532$ nm and focused to a 10 μm spot size. A Renishaw inVia mapping microRaman spectrometer connected to a Leica microscope and equipped with a 325 nm (He-Cd) line-focus laser was used to acquire UV Raman spectra. Wavelength and intensity calibrations were completed by an internal silicon standard using the peak at 520 cm^{-1} . Raman spectra were collected using an 1800 lines/mm grating resulting in resolution $\sim 1\text{ cm}^{-1}$, with 100 s integration time per spectrum, and collected using a CCD array. Spectra were processed and analyzed using Wire 3.2 software and peaks were fitted using mixed Gaussian-Lorentzian curves. All measurements were taken in standard laboratory conditions.

A PHI 5000 Versaprobe imaging X-ray photoelectron spectrometer operating a monochromatic, focused Al K α X-ray source ($E = 1486.6\text{ eV}$) at 25 W with a 100 μm spot size, was used to determine the chemical bonding in the samples. All samples were grounded. Charge neutralization was provided by a cold cathode electron flood gun and by a low-energy Ar⁺ ion gun operating at 110 V accelerating voltage and 5 mA emission current. All measurements were taken under an Ar working pressure of $2 \times 10^{-6}\text{ Pa}$ and room temperature. The system base pressure was $5 \times 10^{-8}\text{ Pa}$. Before surface sputtering, XPS spectra were recorded to avoid the possibility of ion-induced changes in the chemical bonding state of the sample. After sputtering with 500 eV Ar⁺ ions for 3 minutes to remove possible surface contaminations, spectra were

recorded to confirm the chemical composition. Multipak v9.0 software was used to analyze the resulting spectra.

3. Results and Discussion

All DND samples survived both single gas and two-gas plasma treatment for 45 minutes. DND layers were still well-adherent to the substrate which allowed for reasonably easy handling of the material during characterization. X-ray diffraction spectra of the starting and plasma-treated DND did not show the presence of any crystalline or turbostratic graphite phases. Diamond structure also remained mainly intact after exposure to all plasmas as judged by the presence of the (111) peak at 43.9° (Figure 1, peak intensity was not normalized). The application of different peak fitting procedures (Gaussian and Cauchy functions) and crystal size calculations using the Scherrer equation [21,22] revealed an average size of 5.3 nm for the diamond crystallites in the original and H₂ plasma-treated DND. The exposure of DND to O₂ and N₂ plasma resulted in a decrease in (111) peak intensity and width. Because equal quantities of DND were used in each experiment, the decrease of intensity may be associated with the loss of material due to enhanced plasma etching. A small decrease in the width of the (111) peak (calculated crystallite size was 5.9 nm) could be the result of smaller diamond crystallites experiencing a higher etching rate than the larger crystallites within the DND precipitate.

FTIR spectra collected from DND samples treated in single gas plasmas are shown in Figure 2. The original detonation nanodiamond powder showed distinct absorption bands (Fig.2a) at 1560 cm^{-1} (C-H or O-H groups), 1640 cm^{-1} (adsorbed water and C-O-O-H), 1740 cm^{-1} (C=O), a broad band centered around 3400 cm^{-1} (-OH and adsorbed water), broad absorption in the $1400\text{ cm}^{-1} - 1050\text{ cm}^{-1}$ region (e.g., C-H and O-H bending around 1340 , C-O-C at 1258 cm^{-1} , and ester

C-O at 1115 cm^{-1}), and very weak absorbance at 2860 cm^{-1} , 2930 cm^{-1} and 2960 cm^{-1} , associated with stretching vibrations of CH_2 and CH_3 groups [17].

The H_2 plasma treatment at 923 K substrate temperature led to the pronounced enhancement of the CH_x absorption bands in 3000 cm^{-1} - 2800 cm^{-1} region (Fig.2b) which indicates DND surface termination with hydrogen. The bands have been assigned to symmetric and asymmetric vibrations of $\text{sp}^3\text{-CH}_3$ (peaks at 2959 cm^{-1} and 2876 cm^{-1}) and $\text{sp}^3\text{-CH}_2$ (peak at 2930 cm^{-1} and a possible shoulder at 2852 cm^{-1}) groups. The absorption due to $\text{sp}^2\text{-CH}_x$ groups was not observed in the experiments. Two small, but noticeable absorption bands, appeared at 1330 cm^{-1} and 834 cm^{-1} (C-H bending) and the band at 1740 cm^{-1} (C=O) disappeared from the spectrum due to the surface hydrogenation. Disappearance of this characteristic peak at 1740 cm^{-1} could serve as a proof that the entire volume of DND sample reacted with hydrogen plasma species. Absorption bands at 1640 cm^{-1} and 3400 cm^{-1} due to adsorbed water remained practically the same indicating little change in the gas adsorbing properties of H_2 plasma-treated DND. This was verified by recording FTIR spectra of DND at temperatures up to 453 K. Both bands gradually decreased with increasing temperature, whereas other absorption bands remained unchanged.

Exposure of DND to O_2 or N_2 gas plasmas resulted in noticeable C-O and C-N bonding, respectively (Fig.2c-e). Hydrogen was used at the initial stage of those processes to raise the substrate temperature and stabilize O_2 or N_2 plasma. Remarkably, CH_x groups that formed during this initial stage of plasma treatment were not removed by subsequent exposure to oxygen and nitrogen plasma species. O_2 gas plasma treatment (Fig.2c) re-oxidized the DND surface as evident from the enhancement of absorption due to C=O groups (1746 cm^{-1}). The intensity of this band in the FTIR spectrum became relatively stronger than it was in the original DND. On the contrary, N_2 gas plasma treatment (Fig.2d,e) led to the appearance of $\text{-C}\equiv\text{N}$ (2160 cm^{-1} -

2190 cm^{-1}), and other CNH_x groups (in 1580 cm^{-1} - 1100 cm^{-1} region), depending on the substrate temperature. It was suggested that the lack of C=O groups in N_2 plasma-treated DND was associated with H_2 plasma pre-treatment, and thus nitrogen plasma species interacted with mainly oxygen-free DND surface. It was observed that even for relatively small variations in the substrate temperature the result of N_2 plasma modification of DND surface was very different. For example, the FTIR spectrum of N_2 plasma-treated DND in Fig.2d (substrate temperature 1048 ± 25 K) demonstrated strong bands at 1564 cm^{-1} and 1254 cm^{-1} (due to coupled bend-stretch oscillations of C-N-H in the amide group), and other new bands at 1461 cm^{-1} (N-H in plane bending), 1401 cm^{-1} , 1305 cm^{-1} , 1196 cm^{-1} , 1137 cm^{-1} (possibly N-H and C-N stretching in different configurations) and very weak absorption around 2174 cm^{-1} (nitrile group) [23,24]. However, at a slightly higher substrate temperature (1128 ± 25 K), only the nitrile bands around 2160 cm^{-1} dominated (Fig.2e). The formation of nitrile groups can be associated with a sharply increased efficiency of molecular nitrogen dissociation when the substrate temperature exceeds a certain threshold. CH_x absorption bands became broader and weaker in the latter FTIR spectrum, which could be related to the enhanced etching of DND surface layers by atomic nitrogen under these process conditions. A local increase in the concentration of carbon and nitrogen species can lead to the formation of nitrogen-enriched amorphous carbon layer within the porous DND precipitate.

Significant differences in the plasma-treatment results were noted when the DND was exposed to binary gas mixtures, either H_2/O_2 or H_2/N_2 . First, when hydrogen was present, the effect of both O_2 and N_2 gases on DND surface modification was much less. Second, hydrogen seemed to be efficient at higher substrate temperatures in creating more $\text{sp}^3\text{-CH}_3$ groups and stabilizing the surface against oxygen and nitrogen plasma species. Figure 3 shows the

comparison between FTIR spectra of DND treated in single and binary gas plasmas. One difference between the spectra of H₂ plasma-treated DND in Fig.2b and Fig.3a is the relatively higher ratio of sp³-CH₃ to sp³-CH₂ groups. This can be a result of the higher reactivity of hydrogen species at higher substrate temperatures. There were almost no changes in the FTIR spectra of H₂/O₂ or H₂/N₂ plasma-treated DND when compared with the pure H₂ sample, except the appearance of a strong nitrile absorption band at 2177 cm⁻¹ in H₂/N₂ plasma-treated DND [25]. FTIR spectra of N₂ and H₂/N₂ plasma-treated samples in Fig.3d,e were almost identical, which indicates that nitrile groups formation, above the threshold substrate temperature, seems to be independent of the presence of H₂. Formation of less reactive HN₂⁺ and an increased ratio of H/N atoms were proposed in this case [26]. This could increase the etching rate of non-diamond constituents while simultaneously reducing the re-deposition and less affecting the DND core structure. Furthermore, annealing of N₂ and H₂/N₂ plasma-treated DND in air led to the disappearance of nitrile groups above 473 K. This indicates that the nitrogen-rich re-deposited layer may have a polymeric-like structure. FTIR spectra similar to those of the original DND were obtained after annealing these samples at 673 K.

Several possible competing processes involved in the observed trends include the preferential etching of sp²-bonded carbon and DND core stabilization by hydrogen [9, 27], surface etching and removal of reaction products by oxygen, and temperature-dependent etching of DND and formation of polymeric-like fragments by nitrogen plasma species. The formation of, perhaps less reactive to DND, OH_x and NH_y radicals in binary gas plasmas could also lead to a smaller effect of individual gases in the mixture. Besides, it is reasonable to assume that the motion of plasma species was limited within a porous DND precipitate, even though it was a few tens of micrometers thick, leading to the extended residence time of plasma species. In the case

of nitrogen plasma this may have created favorable conditions for the temperature-dependent re-deposition and plasma polymerization of CN_xH_y -rich compounds on the DND surface.

As a companion technique to FTIR, Raman spectroscopy revealed that microwave plasma treatment had, indeed, relatively small effects on the DND core structure for most of the process parameters used. Raman spectra (532 nm laser excitation) recorded from the original and single-gas plasma-treated DND are shown in Figure 4. Based on literature [28], an optimized fitting procedure of the spectra includes five bands (1324 cm^{-1} , 1370 cm^{-1} , 1480 cm^{-1} , 1550 cm^{-1} , 1594 cm^{-1}) in Fig.4a-d, and six bands (1583 cm^{-1} and 1610 cm^{-1} instead of single 1594 cm^{-1} band) in Fig.4e. The ratio R_{pa} of the peak area at 1324 cm^{-1} (assigned to sp^3 -bonds in ND) to a sum of 1550 cm^{-1} and 1594 cm^{-1} peaks (assigned to sp^2 -bonded small carbon clusters and G-band of graphite) serves as a possible indicator of structural changes in DND particles. The values of R_{pa} for Raman spectra in Fig.4a-e were obtained as 0.87, 0.69, 0.63, 0.46, and 0.43, respectively, with the higher number corresponding to a larger amount of sp^3 -bonded phases. This data suggests that N_2 plasma treatment led to somewhat larger sp^2 -bonded carbon content in DND samples, especially at higher temperature, and the H_2 plasma had the least effects.

The observed trend was in good agreement with the results of UV (excitation wavelength 325 nm) Raman spectroscopy (Figure 5). A peak at 1326 cm^{-1} is a characteristic feature of crystalline DND particles in UV Raman spectra, while a broad peak centered at 1646 cm^{-1} is the superposition of Raman bands of sp^2 -bonded carbon, -OH and C=O groups [29]. There was little difference in UV Raman spectra of the original, H_2 and O_2 plasma-treated DND samples. In N_2 plasma-treated samples, the intensity of 1326 cm^{-1} peak is reduced when compared with the peak at 1610 cm^{-1} (Fig.5d). Raman spectrum in Fig.5e (high-temperature N_2 plasma-treated DND) showed a strong narrow peak at 1581 cm^{-1} and a 1400 cm^{-1} peak. The first peak is a

characteristic feature in graphitic materials, and the second peak can be associated with a disorder-induced band in the aromatic sp^2 -carbon clusters [28,30], perhaps at the interface between the diamond and graphitic regions. This indicates significant sp^2 -bonded carbon content when DND samples are treated in an N_2 plasma at 1128 ± 25 K. Raman spectrum of H_2/N_2 plasma-treated DND was identical to that of N_2 DND sample. However, neither 532 nm nor 325 nm Raman spectroscopy registered the presence of C-N bonds in N_2 plasma-treated DND. Possible reasons for this may be the low content of CN_xH_y groups, their weak Raman activity [31], and localized sample heating, especially in the formed sp^2 -rich thin layer, during the Raman experiments [32,33]. It should be emphasized that the nitrile absorption band in FTIR spectra appears strong only due to the reduced peaks from other bands.

XPS data support FTIR and Raman spectroscopy results on the surface modification of plasma-treated DND powders. Table 1 provides a summary of XPS spectral features for all plasma-treated DND. The C/N/O ratios in Table 1 were calculated from C1s, O1s, and N1s peaks in XPS survey spectra shown in Figure 6, and other data were taken from the high-resolution scans of those peaks. It can be seen that plasma treatment in individual gases significantly changes the composition of DND, whereas binary plasmas provided intermediate results. On the other hand, the main peak position of plasmon loss spectra was observed around 34.2 – 34.7 eV (σ -plasmon in bulk diamond) for almost all samples, which confirm their diamond structure, except the high-temperature N_2 plasma-treated sample showing graphitic features [34,35]. High resolution C1s core level (before and after sputtering) and plasmon loss spectra of DND treated in single gas plasmas are shown in Figure 6. XPS data indicate the formation of noticeable amount of sp^2 -bonded carbon only in N_2 plasma-treated DND at higher temperature (Fig.6e), which correlates with the results from Raman spectroscopy. C1s core level peak in this sample is

centered at 285.0 eV with small contributions at approximately 286.0 eV ($\text{-C}\equiv\text{N}$) and 287.4 eV (C-O in adsorbed CO_2). The peak position at 285 eV can be related to either sp^3 -bonded carbon or C-H bonds or bond deformation in very small sp^2 -bonded carbon clusters [36]. The latter feature can also be the reason for the appearance of 1400 cm^{-1} peak in UV Raman spectrum of this sample. Plasmon loss spectrum of this sample exhibits maxima at 27.5 eV ($\pi+\sigma$ plasmon) and 6.5 eV ($\pi-\pi^*$ transition) which are characteristic to graphitic structure. A relatively flat plateau above 27.5 eV can still indicate some overlap with σ -plasmon in very small DND crystallites [34,35]. Furthermore, a weak but resolved N1s peak is centered around 398.1 eV in this sample (Fig.6e, inset), which can be assigned to the both nitrogen bonded to three carbon atoms in sp^2 -configuration and a terminating $\text{-C}\equiv\text{N}$ bonding configuration [37]. The DND sample treated in N_2 at lower temperature exhibited a broad C1s peak (Fig.6d) and a weak but broad N1s peak between 397.4 eV and 400.0 eV (Fig.6d, inset) due to the presence of various CN_xH_y bond configurations. This sample had the highest nitrogen content (4.8 at%). The plasmon loss spectrum of this sample shows the characteristic maximum at 34.5 eV which is similar to plasmon loss spectra of all other DND samples except the more graphitic high-temperature N_2 plasma-treated one. Interestingly, the high-temperature H_2/N_2 plasma-treated DND sample revealed almost the same C1s and plasmon loss spectra (not shown) whereas its FTIR spectrum (Fig.3d) was similar to that of high-temperature N_2 plasma-treated DND. Such difference suggests that hydrogen prevents, at least partially, the graphitization of DND in H_2/N_2 plasma, and the formation of nitrile groups is stimulated at a higher substrate temperature.

The shape and width of C1s core level in binding energy spectra in Fig.6a-d confirmed the presence of multiple chemical bonding types that fit into the typical binding energy ranges for C-H (285 eV – 286 eV), C-N (285.5eV – 286.9 eV), and C-O (286 eV – 289 eV) groups in

different combinations [38,39]. However, the fitting and quantitative analysis of these spectra is complicated by the complexity of bond configurations, and thus the results are discussed rather qualitatively. Although C1s peak at 285 eV is usually assigned to sp^3 C-C bonding, the contributions from CH_x (285 eV – 286 eV) and sp^2 C-C (284.3 eV) bonding, along with rough surface of DND samples and local electric charge transfer, made the determination of sp^3/sp^2 ratio not possible. On the other hand, the observed trends in the C1s peak position and shape correlate with other results on the composition and dominating surface groups in plasma-treated DND, such as the reduction or increase in C-O functional groups in H_2 and O_2 plasma-treated DND (Fig.6b and Fig.6c, respectively), or the graphitization and loss of surface functional groups in high-temperature N_2 plasma-treated DND. Sputtering of the samples with 500 eV Ar^+ ions for 1 minute partially removed the weakly-bonded surface functional groups, reduced the amounts of nitrogen- and oxygen-rich surface groups, and revealed a better defined C1s peak from DND particle core around 285 eV in the original, H_2 , and O_2 plasma-treated samples. There was less change in C1s spectrum of lower-temperature N_2 plasma-treated DND, and very little change in the C1s peak after sputtering high-temperature N_2 plasma-treated DND. This can be due to the presence of a relatively thick CN_xH_y re-deposited layer, which would take a longer time to remove.

4. Conclusions

In summary, detonation nanodiamond particles can be efficiently modified under the microwave plasma conditions in single and binary H_2 , O_2 , and N_2 gas plasmas. The result of such modification depended on the type of plasma species and substrate temperature. DND surface hydrogenation and oxidation were main effects of H_2 and O_2 plasma, respectively, whereas N_2

plasma led to the formation of various CN_xH_y functional groups below 1073 K and nitrile at higher temperatures. Noticeable graphitization of DND was observed only in N_2 plasma at a substrate temperature above 1103 K. Partial re-deposition of etched species and plasma polymerization effects in N_2 plasma were proposed to lead to the formation of nitrogen-rich amorphous surface layer on DND core. It was observed for the first time that hydrogen in H_2/N_2 and H_2/O_2 binary gas plasmas tends to hinder the effects of oxygen and nitrogen plasma species, respectively. These results demonstrated a possibility for broad range tuning of the surface functionality of DND particles, without considerable alteration of their initial structure, with a reasonable level of control by using different gas compositions in microwave discharge plasma.

Acknowledgements

The authors would like to thank Dr. Stanislaw Mitura for providing DND powders, Dr. Molly Gentleman for the help with UV Raman spectroscopy, and Inessa Stanishevskaya for graphics design. FTIR and XPS spectroscopy instruments used in this research were supported by the National Institutes of Health - National Center for Research Resources (NIH/NCRR) Grant S10RR023388 and by NSF Grant DRM-0922910, respectively.

References

1. N.R. Greiner, D.S. Phillips, J.D. Johnson, F. Volk, Diamonds in detonation soot, *Nature* 333 (1988) 440-442.
2. A.S. Artemov, Polishing nanodiamonds, *Phys. Solid State* 46 (2004) 687-695.

3. O. Shenderova, C. Jones, V. Borjanovic, S. Hens, G. Cunningham, S. Moseenkov, V. Kuznetsov, G. McGuire, Detonation nanodiamond and onion-like carbon: applications in composites, *Phys. Stat. Sol. A* 205 (2008) 2245-2251.
4. K.D. Behler, A. Stravato, V. Mochalin, G. Korneva, G. Yushin, Y. Gogotsi, Nanodiamond-Polymer Composite Fibers and Coatings, *ACS Nano* 3 (2009) 363-369.
5. R.A. Shimkunas, E. Robinson, R. Lam, S. Lu, X. Xu, X.Q. Zhang, H. Huang, E. Osawa, D. Ho, Nanodiamond–insulin complexes as pH-dependent protein delivery vehicles, *Biomaterials* 30 (2009) 5720-5728.
6. T. Burleson, N. Yusuf, A. Stanishevsky, Surface Modification of Nanodiamonds for Biomedical Application, *J. Achiev. Mater. Manuf. Eng.* 37 (2009) 258-263.
7. C.C. Fu, H.Y. Lee, K. Chen, T.S. Lim, H.Y. Wu, P.K. Lin, P.K. Wei, P.H. Tsao, H.C. Chang, W. Fann, Characterization and application of single fluorescent nanodiamonds as cellular biomarkers, *Proc. Natl. Acad. Sci. U.S.A.* 104 (2007) 727-732.
8. A. Krueger, D. Lang, Functionality is key: Recent progress in the surface modification of nanodiamond, *Adv. Funct. Mater.* 22 (2012) 890-906.
9. V.Yu. Dolmatov, Detonation-synthesis nanodiamonds: synthesis, structure, properties and applications, *Russian Chem. Rev.* 76 (2007) 339-360.
10. A. Kruger, F. Kataoka, M. Ozawa, T. Fujino, Y. Suzuki, A.E. Alesenskii, A.Y. Vul, E. Osawa, Unusually tight aggregation in detonation nanodiamond: Identification and disintegration, *Carbon* 43 (2005) 1722-1730.
11. Q. Yu, Y.J. Kim, H. Ma, Plasma treatment of diamond nanoparticles for dispersion improvement in water, *Appl. Phys. Lett.* 88 (2006) 231503.

12. N. Gibson, O. Shenderova, T.J.M. Luo, S. Moseenkov, V. Bondar, A. Puzyr, K. Purtov, Z. Fitzgerald, D.W. Brenner, Colloidal stability of modified nanodiamond particles, *Diamond Relat. Mater.* 18 (2009) 620-626.
13. J.H.C. Yang, K. Teii, Mechanism of enhanced wettability of nanocrystalline diamond films by plasma treatment, *Thin Solid Films* 520 (2012) 6566-6570.
14. S. Su, J. Li, V. Kunderát, A.M. Abbot, H. Ye, Hydrogen-passivated detonation nanodiamond: An impedance spectroscopy study, *Diamond Relat. Mater.* 24 (2012) 49-53.
15. M.A. Ray, O. Shenderova, W. Hook, A. Martin, V. Grishko, T. Tyler, G.B. Cunningham, G. McGuire, Cold plasma functionalization of nanodiamond particles, *Diamond Relat. Mater.* 15 (2006) 1809-1812.
16. H.A. Girard, J.C. Arnault, S. Perruchas, S. Saada, T. Gacoin, J.-P. Boilot, P. Bergonzo, Hydrogenation of nanodiamonds using MPCVD: A new route toward organic functionalization, *Diamond Relat. Mater.* 19 (2010) 1117-1123.
17. H. Kozak, Z. Remes, J. Houdkova, S. Stehlik, A. Kromka, B. Rezek, Chemical modifications and stability of diamond nanoparticles resolved by infrared spectroscopy and Kelvin force microscopy, *J. Nanoparticle Res.* 15 (2013) 1568.
18. X. Liu, Z. Yu, Q. Wei, G. Wen, X. Duan, X. You, Modification of polycrystalline nanodiamonds by using periodic magnetic field enhanced hydrogen plasma and the application on nanogrinding of thin film magnetic head, *Colloid. Surf. A* 416 (2013) 9-15.
19. J.C. Arnault, T. Petit, H. Girard, A. Chavanne, C. Gesset, M. Sennour, and M. Chaigneau, Surface chemical modifications and surface reactivity of nanodiamonds hydrogenated by CVD plasma, *Phys. Chem. Chem. Phys.* 13 (2011) 11481–11487.

20. J.C. Arnault, S. Saad, M. Nesladek, O.A. Williams, K. Haenen, P. Bergonzo, E. Osawa, Diamond nanoseeding on silicon: Stability under H₂ MPCVD exposures and early stages of growth, *Diamond Relat. Mater.* 17 (2008) 1143-1149.
21. S.V. Tsybulya, S.V. Cherepanova, G.N. Kryukova, Full profile analysis of X-ray diffraction patterns for investigation of nanocrystalline systems, in *Diffraction analysis of the microstructure of materials*, Eds. E.J. Mittemeijer, P. Scardi, Springer, Berlin, 2004, pp.93-123.
22. B. Palosz, E. Grzanka, C. Pantea, T.W. Zerda, Y. Wang, J. Gubicza, T. Ungár, Microstructure of nanocrystalline diamond powders studied by powder diffractometry, *J. Appl. Phys.* 97 (2005) 064316.
23. P.J. Larkin, *Infrared and Raman spectroscopy; Principles and spectral interpretation*, Elsevier, Oxford, 2011, p.69.
24. D. Lin-Vien, N.B. Colthup, W.G. Fateley, J.G. Grasselli, *The handbook of infrared and Raman characteristic frequencies of organic molecules*, Academic Press, London, 1991, pp.167-169.
25. A. Majumdar, G. Das, K.R. Basvani, J. Heinicke, R. Hippler, Role of Nitrogen in the Formation of HC-N Films by CH₄/N₂ Barrier Discharge Plasma: Aliphatic Tendency, *J. Phys. Chem. B* 113 (2009) 15734.
26. E. Tatarova, V. Guerra, J. Henriques, C.M. Ferreira, Nitrogen dissociation in low-pressure microwave, *J. Phys. Conf. Ser.* 71 (2007) 012010.
27. Z. Shpilman, I. Gouzman, E. Grossman, R. Akhvediani, A. Hoffman, Hydrogen plasma and atomic oxygen treatments of diamond: chemical versus morphological aspects, *Appl. Phys. Lett.* 92 (2008) 234103.

28. A.C. Ferrari, J. Robertson, Raman spectroscopy of amorphous, nanostructured, diamond-like carbon, and nanodiamond, *Phil. Trans. R. Soc. Lond. A* 362 (2004) 2477-2512.
29. V. Mochalin, S. Osswald, Y. Gogotsi, Contribution of functional groups to the Raman spectrum of nanodiamond powders, *Chem. Mater.* 21 (2009) 273-279.
30. A.C. Ferrari, J. Robertson, Resonant Raman spectroscopy of disordered, amorphous, and diamondlike carbon, *Phys. Rev. B* 64 (2001) 075414.
31. A.C. Ferrari, S.E. Rodil, J. Robertson, Interpretation of infrared and Raman spectra of amorphous carbon nitrides, *Phys. Rev. B* 67 (2003) 155306.
32. M. Liu, K.L. Jiang, Q.Q. Li, H.T. Yang, S.S. Fan, Laser-induced high local temperature in carbon nanotube, *Solid State Phenom.* 121-123 (2007) 331-336.
33. J. Vlček, P. Fitl, M. Vrnata, L. Fekete, A. Taylor, F. Fendrych, UV-laser treatment of nanodiamond seeds - a valuable tool for modification of nanocrystalline diamond films properties, *J. Phys. D: Appl. Phys.* 46 (2013) 035307.
34. X. Liu, F. Klauser, N. Memmel, E. Bertel, T. Pichler, M. Knupfer, A. Kromka, D. Steinmüller-Nethl, Spectroscopic studies of nanocrystalline diamond materials, *Diam. Relat. Mater.* 16 (2007) 1463–1470.
35. S. Zeppilli, J.C. Arnault, C. Gesset, P. Bergonzo, R. Polini, Thermal stability and surface modifications of detonation diamond nanoparticles studied with X-ray photoelectron spectroscopy, *Diam. Relat. Mater.* 19 (2010) 846-853.
36. Yu.V. Butenko, S. Krishnamurthy, A. K. Chakraborty, V.L. Kuznetsov, V.R. Dhanak, M.R.C. Hunt, L. Šiller, Photoemission study of onionlike carbons produced by annealing nanodiamonds, *Phys. Rev. B* 71 (2005) 075420.

37. J. C. Sánchez-López, C. Donnet, F. Lefèbvre, C. Fernández-Ramos and A. Fernández, Bonding Structure in Amorphous Carbon Nitride: A Spectroscopic and Nuclear Magnetic Resonance Study, *J. Appl. Phys.* 90 (2001) 675-681.
38. Sh. Michaelson, R. Akhvlediani, T. Petit, H.A. Girard, J.C. Arnault, A. Hoffman, HR-EELS study of hydrogen bonding configuration, chemical and thermal stability of detonation nanodiamond films, *Appl. Surf. Sci.* 305 (2014) 160–166.
39. S. Torrenzo, R. Canteri, R. Dell’Anna, L. Minati, A. Pasquarelli, G. Speranza, XPS and ToF-SIMS investigation of nanocrystalline diamond oxidized surfaces, *Appl. Surf. Sci.* 276 (2013) 101–111.

Table 1. Summary of XPS data on original and microwave plasma-treated DND particles

Material and process	C/O/N ratio, at%	C1s, eV	Plasmon Loss ΔE, eV	N1s,eV	O1s, eV
(a) original ND	90.1/7.3/2.6	287.1; 287.9	34.7	401.0	533.4
(b) H ₂ plasma T _s =923±10K	94.2/4.8/1.0	285.9; 286.5; 287.4	34.5	400.0 trace	532.3
(c) O ₂ plasma T _s =703±10K	73.7/21.6/2.4	285.8; 287.8	34.2	401.0 trace	532.7; 530.9
(d) N ₂ plasma T _s =1048±25 K	84.6/8.0/4.7	285.9; 287.0; 287.6	34.2	397.4 – 400.0 Broad peak	532.0; 530.9
(e) N ₂ plasma T _s =1128±25 K	94.2/3.0/2.8	285.0; 286.0; 287.4	6.5 and 27.5	398.1	532.4
(f) H ₂ /N ₂ plasma, T _s =1128±25 K	91.7/4.9/3.4	285.8; 286.4; 287.4	34.4	398.2	532.4
(g) H ₂ /O ₂ plasma, T _s =1033±25 K	89.4/9.4/1.2	285.9; 286.6; 287.8	34.5	400.0 trace	532.5

FIGURE CAPTIONS

Figure 1. X-ray diffraction patterns of (a) original detonation nanodiamond (DND) powder, and DND exposed to microwave gas plasma of (b) H₂ at T_s= 923±10 K, (c) O₂ at T_s= 703±10 K, (d) N₂ at T_s= 1048±25 K, and (e) N₂ at T_s= 1128±25 K.

Figure 2. FTIR spectra of (a) original detonation nanodiamond (DND) powder, and DND exposed to microwave gas plasma of (b) H₂ at T_s= 923±10 K, (c) O₂ at T_s= 703±10 K, (d) N₂ at T_s= 1048±25 K, and (e) N₂ at T_s= 1128±25 K. Expanded view of CH_x absorption bands in 2800 cm⁻¹ – 3000 cm⁻¹ infrared region is shown on the right.

Figure 3. FTIR spectra of DND exposed to microwave gas plasma of (a) H₂ at T_s= 1013±10 K, (b) H₂/O₂ at T_s= 1033±25 K, (c) O₂ at T_s= 703±10 K, (d) N₂ at T_s= 1128±25 K, and (e) H₂/N₂ at T_s= 1128±25 K. Expanded view of CH_x absorption bands in 2800 cm⁻¹ – 3000 cm⁻¹ infrared region is shown on the right.

Figure 4. Raman spectra (532 nm) of (a) original DND powder, and DND exposed to microwave gas plasma of (b) H₂ at T_s= 923±10 K, (c) O₂ at T_s= 703±10 K, (d) N₂ at T_s= 1048±25 K, and (e) N₂ at T_s= 1128±25 K. The lines at 1332 cm⁻¹ and 1581 cm⁻¹ are provided to guide the eye. Peak fitting for original DND (left), and DND treated in N₂ plasma at temperature 1128±25 K (right) are shown below.

Figure 5. UV Raman spectra (325 nm) of (a) original detonation nanodiamond (DND) powder, and DND exposed to microwave gas plasma of (b) H₂ at T_s= 923±10 K, (c) O₂ at T_s= 703±10 K, (d) N₂ at T_s= 1048±25 K, and (e) N₂ at T_s= 1128±25 K. The lines at 1326 cm⁻¹ and 1646 cm⁻¹ are provided to guide the eye.

Figure 6. XPS survey spectra of all plasma-treated samples (top), N1s (top inset) and C1s core energy level (middle, before and after sputter cleaning with 500 eV Ar⁺ ions for 1 minute), and plasmon loss (bottom, no sputter cleaning) spectra of DND samples treated in single gas plasma: (a) original detonation nanodiamond (DND) powder, and DND exposed to microwave gas plasma of (b) H₂ at T_s= 923±10 K, (c) O₂ at T_s= 703±10 K, (d) N₂ at T_s= 1048±25 K, (e) N₂ at T_s= 1128±25 K, (f) H₂/N₂ at T_s=1128±25 K, and (g) H₂/O₂ plasma, T_s=1033±25 K.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6