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## Microwave plasma-assisted photoluminescence enhancement in nitrogen-doped ultrananocrystalline diamond film

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Optical properties and conductivity of nitrogen-doped ultrananocrystal diamond (UNCD) films were investigated following treatment with low energy microwave plasma at room temperature. The plasma also generated vacancies in UNCD films and provided heat for mobilizing the vacancies to combine with the impurities, which formed the nitrogen-vacancy defect centers. The generated color centers were distributed uniformly in the samples. The conductivity of nitrogen-doped UNCD films treated by microwave plasma was found to decrease slightly due to the reduced grain boundaries. The photoluminescence emitted by the plasma treated nitrogen-doped UNCD films was enhanced significantly compared to the untreated films. *Copyright 2012 Author(s). This article is distributed under a Creative Commons Attribution 3.0 Unported License.* [<http://dx.doi.org/10.1063/1.4727743>]

In recent years, in addition to quantum emitters, classical light sources base on luminescence from color centers in diamond have generated great interest for biomedical applications such as optical labels.<sup>1-3</sup> Nitrogen is the most prominently known impurity, and forms the nitrogen vacancy defect in diamond. This defect consists of substituting a nitrogen atom with the nearest vacancy. According to whether the impurities close to the surrounding area act as electron donor or acceptor, the defects can form two types of states: neutral nitrogen vacancy center [(N-V)<sup>0</sup>] and negative-charged nitrogen vacancy center [(N-V)<sup>-</sup>]. [(N-V)<sup>0</sup>] center has a nominal C<sub>3v</sub> symmetry and zero-phonon E-A optical transition at 575nm. The [(N-V)<sup>-</sup>] center has been identified with a zero-phonon 637nm corresponding to a <sup>3</sup>A-<sup>3</sup>E transition and site symmetry C<sub>3v</sub>. The model for neutral and negative charged N-V center in diamonds has been fully discussed.<sup>4-7</sup>

Recently, the ultrananocrystalline diamond (UNCD) films grown from hydrogen-poor Ar/CH<sub>4</sub> microwave plasmas have attracted much attention as a promising material due to their unique and advantageous properties, such as hardness, chemical inertness, high electron field emission, and possibility of p- and n-type conductivities by doping.<sup>8-10</sup> Moreover, many of these physical properties, such as electrical conductivity, field emission threshold voltage, and mechanical and optical properties, differ from other conventional diamond films.<sup>9,11-13</sup> Several properties of UNCD films indicate dependence on crystalline size, fraction of carbon atoms, and concentration of impurities, which open up scientific and technological applications including optics, microelectronics systems, and tribology.<sup>14,15</sup>

Nitrogen-doped UNCD films synthesized using microwave plasma CVD showed enhancement in electrical conductivity by orders of magnitude with increasing nitrogen content.<sup>11</sup> In contrast to the case of nitrogen in microcrystalline diamond films, which usually forms a deep donor level

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with an activation energy of 1.7 eV, nitrogen is favored by 3-5 eV for grain boundary doping in UNCD.<sup>16,17</sup> Therefore, grain-boundary conduction was proposed by Bhattacharyya *et al.*<sup>11</sup> to explain the remarkable transport properties of nitrogen-doped UNCD films.

Although there are investigations in the vibrational properties of nitrogen-doped UNCD, however, up until now no evidence of nitrogen-related defects in UNCD films has been reported using luminescence spectroscopy.<sup>18-21</sup> Nitrogen-doped UNCD thin films, which show lack of photoluminescence from typical N-V centers found in diamond nanoparticles, indicate that most nitrogen is incorporated as single substitution atoms instead of being trapped as N-V complexes.<sup>4-7</sup> In this report, we demonstrate a simple technique to efficiently incorporate nitrogen with vacancy and generate fluorescence defect centers in nitrogen-doped UNCD films at room temperature, which only requires low power and low energy microwave radiation.

Nitrogen-doped ultrananocrystalline diamond films were grown on SiO<sub>2</sub>/Si substrates in microwave plasma enhanced chemical vapor deposition (MPECVD) system (IPLAS Cyranus) with microwave power of 1400W, a pressure of 110 Torr, and a substrate temperature of 800 °C for 45 minutes. Before the deposition, the substrates were seeded in an ultrasonic bath with nanodiamond particles from detonation synthesis (average size 4-6nm). The Ar-rich mixture gases (73% Ar / 25% N<sub>2</sub> / 2% CH<sub>4</sub>) were used as reaction gases during growth. A thin layer of UNCD film with a thickness of approximately 1 μm was formed on the template.

Figure 1 shows the high-resolution transmission electron microscope (HRTEM) image of the nitrogen-doped UNCD film. The crystalline grain of the nanodiamond indicates a pin-like structure, which is wrapped by the SP<sup>2</sup> C-C bondings. For low-nitrogen partial pressure, the morphology of the films remains largely unchanged, with the grain size and grain boundary (GB) widths increasing only slightly. However, at high nitrogen partial pressure (> 10%), both the grain size and GB widths increase significantly.<sup>22-24</sup> The clustering of larger grains leads to the elongation of the nanocrystalline structures and eventually results in the formation of pin-like structures in the nitrogen-doped UNCD films.

Hall measurements of the samples indicate that electrons are the majority carriers with a density of approximately 10<sup>20</sup> cm<sup>-3</sup> and a carrier mobility of 16 cm<sup>2</sup>/Vs. The electrical conductivity is approximately 140 Ω<sup>-1</sup>cm<sup>-1</sup> for the 25% nitrogen-doped UNCD film at room temperature based on the four-point-probe measurements. It has been proposed that the nearest-neighbor hopping or other thermally activated conduction mechanisms would occur in the GBs and result in greatly enhanced electron transport.<sup>11,25,26</sup>

The Raman spectra for the undoped and nitrogen-doped UNCD films at the excitation wavelength of 488 nm are given in Figures 2(a) and 2(b). The Raman spectrum of the undoped UNCD consists of five peaks, which indicates the characteristics of three different carbon phases: (1) diamond (at 1332 cm<sup>-1</sup>), (2) amorphous SP<sup>2</sup> carbon (D-band at 1350 cm<sup>-1</sup> and G-band at 1550 cm<sup>-1</sup>), and (3) polyacetylene (at 1150 cm<sup>-1</sup> and 1480 cm<sup>-1</sup>).<sup>18-20</sup> The reduction of the crystallinity as the nitrogen is introduced into UNCD films is clearly indicated by the disappearance of the diamond (at 1332 cm<sup>-1</sup>, indicated by arrows in Figures 2(a) and 2(c)) and polyacetylene peaks (1150 cm<sup>-1</sup> and 1480 cm<sup>-1</sup>) in the spectrum of the nitrogen-doped UNCD films. As shown in Figure 2(b), the diamond peak becomes invisible on top of the D-band. The changes in relative intensity between D- and G-band and the shifting of the position of the G-band to higher wave numbers (from 1550 cm<sup>-1</sup> to 1565 cm<sup>-1</sup>) are clear indications of the noticeable changes in the content of the amorphous SP<sup>2</sup> carbon in the films.<sup>21</sup>

The nitrogen-doped UNCD film was treated by microwave plasma with a power of 800 W, total pressure 10 Torr, and at a substrate temperature of 300 K for 30 minutes. The simulated air (80% N<sub>2</sub> / 20% O<sub>2</sub>) was used as the reaction gas during microwave plasma treatment. The inset in Figure 1 shows the HRTEM image of nitrogen-doped UNCD film following treatment. This image illustrates that the morphology of the film remains largely unchanged, and that no re-growth is observed after microwave treatment due to the low radiation power and energy. The conductivity of the nitrogen-doped UNCD film after microwave plasma treatment is only decreased slightly (dropped a fraction of 1 Ω<sup>-1</sup>cm<sup>-1</sup>). Judged by the evidence of reduction of SP<sup>2</sup> carbon phase in the Raman spectra, we attribute it to the slightly etching of the grain boundaries following treatment.

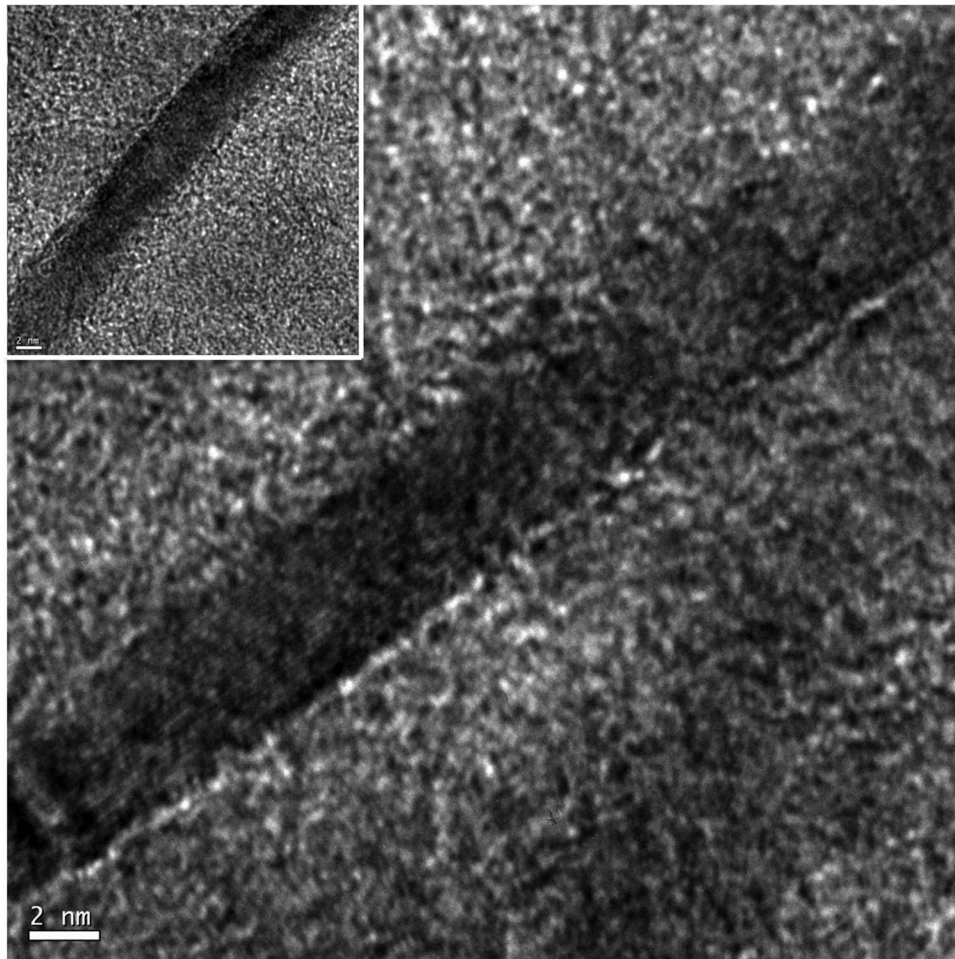


FIG. 1. The HRTEM image of the 25% nitrogen-doped UNCD film. The inset shows the HRTEM image of the film after plasma treatment.

Figure 2(c) shows the Raman spectrum of nitrogen-doped UNCD films after microwave plasma radiation. After the microwave plasma treatment, the intensity of the Raman peaks as the amorphous carbon (D-band and G-band) is strongly attenuated due to the oxidation of the  $SP^2$  carbon cluster by the oxygen in the reaction gases. Therefore, the peak of the diamond at  $1332\text{ cm}^{-1}$  can be clearly revealed. However, under high microwave power ( $> 1400\text{ W}$ ) and total pressure ( $\sim 100\text{ Torr}$ ), both the amorphous carbon and diamond become over etched and their corresponding Raman peak intensities are strongly attenuated, as shown in Figure 2(d).

The nitrogen-doped UNCD samples before and after plasma treatment were examined with an energy dispersive spectrometer (EDS) and secondary ion mass spectrometer (SIMS). The EDS and SIMS spectra are provided in Figures 3(a) and 3(b), respectively. It is noted that EDS and SIMS spectra, as shown in Figure 3, taken from inside the grains of samples before plasma treatment show traces of nitrogen. However, samples without plasma treatment show extremely weak or a complete lack of photoluminescence from typical N-V centers found in the nanodiamonds.<sup>27</sup> The PL spectrum of the nitrogen-doped UNCD film treated with microwave plasma is shown in Figure 4(a). The spectrum of the sample without plasma treatment, as shown in Figure 4(b), is also displayed in parallel for comparison. The two peaks at 522 nm and 528 nm are attributed to the Raman peaks of D-band and G-band. In Figure 4, the PL spectra between 550 nm and 750 nm can be fitted with two major peaks at 575 nm and 630 nm, respectively. Therefore, the emissions between 550 nm and 750 nm originate from the  $[(N-V)^0]$  and  $[(N-V)^-]$ .<sup>4-7</sup> Note that the integrated PL intensity between

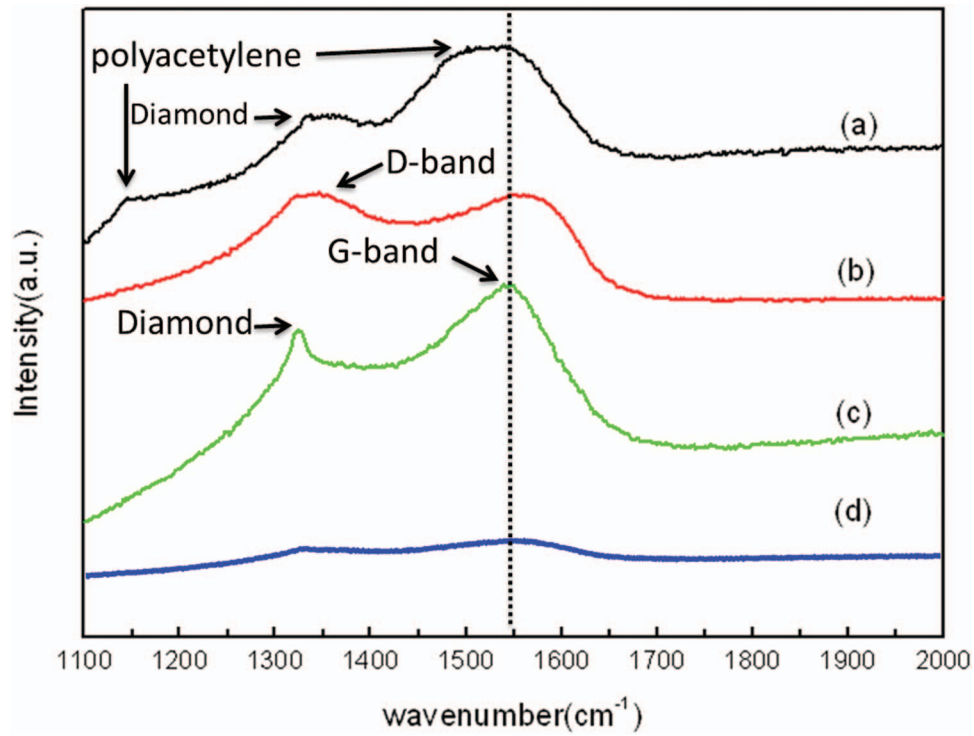


FIG. 2. The Raman spectra of (a) undoped UNCD film (b) nitrogen-doped UNCD film (c) plasma-treated nitrogen-doped UNCD film and (d) plasma-treated nitrogen-doped UNCD under high microwave power and total pressure. The dash line at  $1550 \text{ cm}^{-1}$  (center of the G-band) is to aid the viewing of the figure.

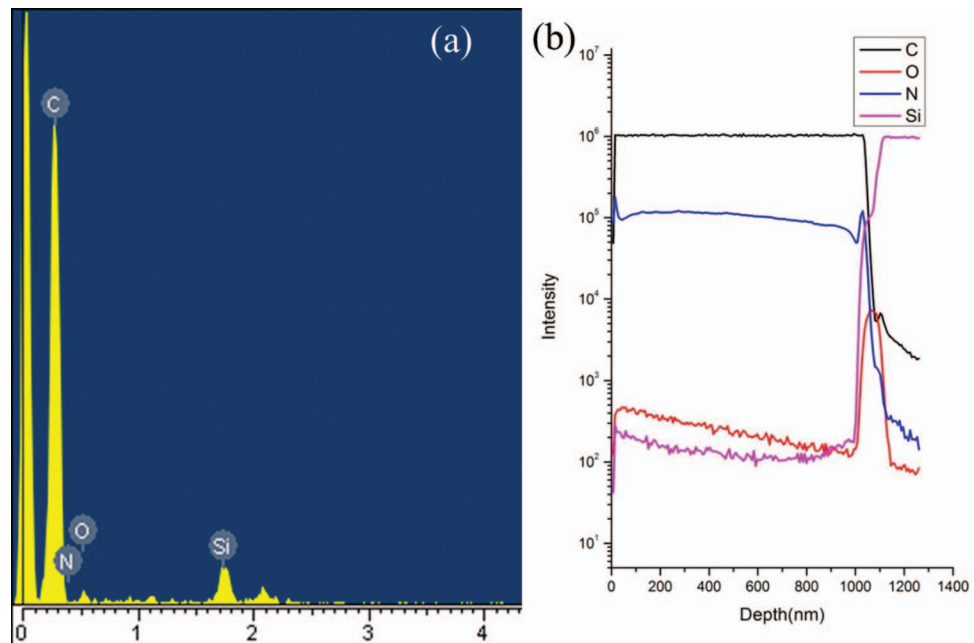


FIG. 3. The spectra of (a) EDS and (b) SIMS from nitrogen-doped UNCD films without plasma treatment.

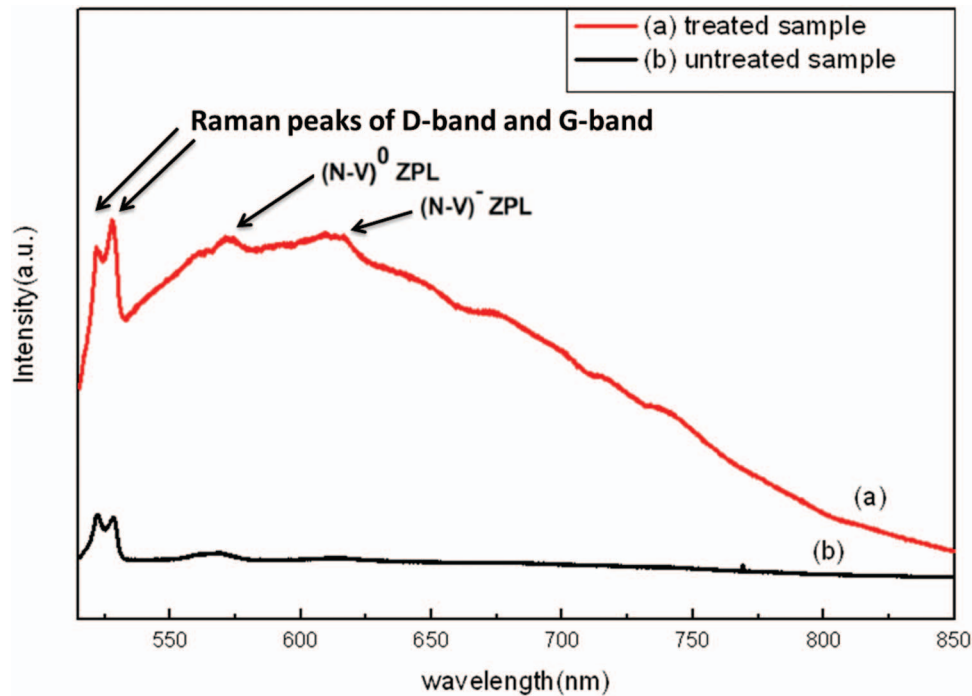


FIG. 4. The photoluminescence spectra of nitrogen-doped UNCD film (a) with and (b) without microwave plasma treatment.

550 nm and 750 nm of plasma-treated samples are greatly enhanced by more than two orders of magnitude in comparison to the untreated samples.

One common technique to create defect centers in diamonds uses ion implantation and high temperature annealing.<sup>28,29</sup> This can also be used to introduce impurities. Following implantation, annealing is performed at a temperature in which vacancies become mobile and combine with impurities to form defect centers. Collins *et al.* confirmed that the emission at 737 nm due to the defect center involving silicon by implanting conventional diamond with Si ions.<sup>30</sup> Meijer *et al.* have shown that nitrogen-vacancy (N-V) defect centers were also produced in very pure diamond (type IIa) by nitrogen implantation as reported in Ref. 29. The N-V defect centers have also been produced in nitrogen-rich diamond (type Ib) by high-energy radiation damage such as focus ion beam (FIB) or electron beam, followed by an annealing process.<sup>28</sup> Here we demonstrate that the microwave plasma treatment with sufficient low energy can also generate the fluorescent defect centers in nitrogen-doped UNCD films even at room temperature. We infer that the microwave plasma may produce vacancies in UNCD films and also generate heat, thereby inducing the movement of the vacancies and combining with impurities to form vacancy centers.

The distribution of generated fluorescent defect centers as a function of depth was found by the micro-PL mapping technology using a confocal microscope. First, we created a stepped slope on the nitrogen-doped UNCD film by cutting the films with a focus ion beam to expose the film at different depth. The scanning electron microscopy (SEM) image of the slope is shown in Figure 5(a). One-dimension PL mapping was carried out on the slope along the red line indicated in Figure 5(a). The PL mapping was scanned along a distance of 7  $\mu\text{m}$  with a step of 300 nm. The integrated PL intensity from the 550 nm to 750 nm PL peaks as a function of the scanning distance plotted in Figure 5(b) at an excitation wavelength of 488 nm. The mapping results indicated that the integrated PL intensity varied linearly with the depth, which implies a uniform distribution of the N-V defect centers inside the nitrogen-doped UNCD film after plasma treatment.

In conclusion, we demonstrate a lower power and lower temperature means of generating fluorescence defect centers in nitrogen-doped UNCD films using microwave plasma. The microwave plasma generates the vacancies due to slightly etching the diamond. The ion gases in the plasma

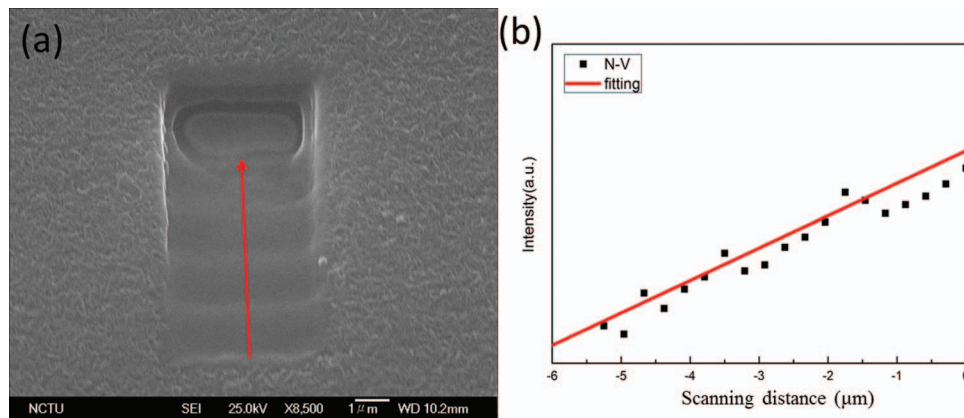


FIG. 5. (a) The SEM image of the slope created on the UNCD film using a focused ion beam (b) The integrated PL intensity between 550 nm and 750 nm as a function of scanning distance.

provide the heat and further mobilize the vacancies to combine with the impurities, which leads to the formation of the N-V. The conductivity of the UNCD film decreases slightly due to the reduced grain boundaries. The PL mapping results show that the plasma generated N-V is uniformly distributed in the nitrogen-doped UNCD film. Fabrication of diamond light-emitting source can be further developed using electrically active color centers in the future.

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