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Electrical conductivity of thermally hydrogenated nanodiamond powders

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Electrical properties of detonation diamond nanoparticles (NDs) with individual diameters of ~5 nm are important for many applications. Although diamond is an insulator, it is known that hydrogen-terminated bulk diamond becomes conductive when exposed to water. We show that heating ND in hydrogen gas at 600–900 °C resulted in a remarkable decrease in resistivity from 10^7 to 10^5 Ω cm, while the resistivity was essentially unchanged after treatment at 400 °C and lower temperatures. Fourier Transform Infrared Spectroscopy and X-ray photoelectron spectroscopy (XPS) studies revealed that hydrogenation of ND occurs at 600–900 °C, suggesting that the decrease in resistivity is based on transfer doping at the hydrogenated ND surface. Oxidation of the hydrogenated sample at 300 °C recovers resistivity to its original value. The resistivity of treated ND as a function of the O/C atomic ratio showed a transition from resistive (O/C ratio < 0.033) to conductive (O/C ratio > 0.033) state. This is consistent with the idea that the change in the resistivity is caused by the shift of the valence band maximum to above the Fermi level due to the dipole of the C-H bonds leading to transfer doping. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4809549]

I. INTRODUCTION

Diamond nanoparticles (NDs) fabricated by detonation of explosives have superior chemical stability, hardness, and biocompatibility.1 Based on these excellent properties, many applications of NDs are being developed in the fields of nanocomposites,2–5 electrochemical energy storage,6 biological fluorescent probes,7–10 and drug delivery carriers.11–13 Nanoparticles have a very high surface-to-volume (surface-to-weight) ratio; therefore, they exhibit surface-dependent properties more prominently than their bulk counterparts. Diamond surface can be modified by various treatments, including dry (thermal and plasma) and wet (chemical, electrochemical, and photochemical) techniques.14 Hydrogenated diamond surfaces are known to exhibit unique properties including hydrophobicity15,16 and, in the case of powder, a high positive zeta potential.17 Negative electron affinity18,19 and surface conductivity20 were also reported for hydrogenated diamond. Surface conductivity of hydrogenated diamond has been explained via the transfer doping mechanism: electron transfer from the valence band of the hydrogenated diamond to the redox species in the electrolyte (adsorbed water) results in accumulation of holes on the diamond surface. This allows two-dimensional electric conduction.20–22 Since ND has a much higher surface-to-volume ratio compared to bulk diamond, the effect of surface hydrogenation of ND on its conductivity should be even more pronounced than for bulk diamond. Recently, Su et al. reported that hydrogenation of detonation ND by hydrogen plasma treatment increased the electrical conductivity, as estimated by impedance spectroscopy, by four orders of magnitude.23 In the present study, we investigated the surface hydrogenation of NDs by high temperature treatment in hydrogen gas and the resistivity of the NDs as a function of treatment temperature. Based upon the estimation of the surface oxygen content and the sp²/sp³ carbon ratio of the treated NDs, the decrease in the resistivity was found to be consistent with the transfer doping caused by the surface hydrogenation of ND.

II. EXPERIMENTAL

The ND used in this study (UD90, nominal particle diameter 5 nm) was provided by Nanoblox, Inc., USA. The UD90 was first oxidized in air in a muffle furnace at 430 °C for 5 h to remove the non-diamond carbon from the particle surface.24,25 The oxidized ND was then refluxed in a mixture of concentrated hydrochloric and nitric acids at 100 °C for 24 h to remove metallic impurities. The purified ND was obtained by pipetting out the supernatant of the acidic aqueous dispersion and adding fresh deionized water in steps until the supernatant became neutral, and drying the powder. The purified ND (denoted here as UD90p) was heated in hydrogen gas atmosphere using a quartz tube furnace at a fixed temperature (200–900 °C) for 1 h. After the heat was turned off, the sample was kept under hydrogen atmosphere until the furnace temperature dropped to below 100 °C. The UD90p after the heat treatment (denoted as H-ND) was characterized by Fourier Transform Infrared Spectroscopy (FTIR in KBr disks; Excalibur FTS-3000, Varian) and X-ray photoelectron spectroscopy (XPS; Axisnova, Kratos). The XP spectra were calibrated by assigning the C 1s peak position

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to be 284.8 eV. The O/C atomic ratio of the ND samples was estimated by quantitative XPS analysis. The $sp^2/sp^3$ carbon ratio of the ND sample was estimated by peak deconvolution of the XPS C 1 s spectra with Gaussian band profiles. The resistivity of ND was calculated from the $I$-$V$ curves of ND packed in a glass tube (inner diameter 1 mm). Both ends of the ND cylinder inside the tube were pressed with copper wires which were connected to the power source. The applied voltage oscillated between $-5$ and $+5$ V at a rate of 5 V s$^{-1}$, and the electric resistance was calculated from the slope of the $I$-$V$ curve in the range of $-1$ to $+1$ V.

III. RESULTS AND DISCUSSION

A. Characterization of hydrogenated ND

The effect of hydrogenation temperature on the surface chemical structure of H-NDs was investigated by FTIR and XPS. Figure 1(a) shows FTIR spectra of the H-NDs treated at 400–900 °C. The spectrum for the sample after hydrogenation at 400 °C showed a band of the C=O stretching mode at 1750 cm$^{-1}$.

The hydrogenation of UD90p was also investigated with XPS by monitoring the content of oxygen, which is substituted with hydrogen as hydrogenation progresses. Figure 2(a) shows XP spectra of H-NDs treated at 400 and 900 °C. The spectra for the H-ND sample treated at 400 °C showed an O 1 s peak at 530 eV. The O 1 s peak was less prominent for the H-ND (900 °C) than for the H-ND (400 °C). The O/C atomic ratio estimated from the XP quantitative analysis plotted as a function of hydrogenation temperature in Fig. 2(b). The O/C ratio of 0.38 for H-ND (400 °C) indicates high oxygen content on the surface. In comparison, the O/C ratio of an oxygen plasma-treated diamond surface was reported to be 0.18. The O/C ratio decreased as the hydrogenation temperature increased from 400 °C to 600 °C, consistent
with Williams et al., and then remained constant (<0.02) at 600–900 °C. Thus, the range of temperatures corresponding to hydrogenation of ND is 600–900 °C, which is consistent with the FTIR results (Fig. 1).

Figures 3(a) and 3(b) show XPS C 1s spectra of H-ND (400 °C) and H-ND (900 °C), respectively. The C1s peaks were fit by four Gaussian profiles corresponding to C=C (283.5 eV), C-C and C-H (284.8 eV), C-O (286.5 V), and C=O (288.5 eV). The intensity of the C=O peak (288.5 eV) in H-ND (900 °C) is slightly lower compared to H-ND (400 °C), while the intensity of C-O (286.5 eV) is much higher in H-ND (900 °C) compared to H-ND (400 °C) due to reduction of C=O into C-OH, in agreement with FTIR data (Fig. 1). The sp²/sp³ carbon ratio, estimated from the area of the peaks at 283.5 eV (C=C) and 284.8 eV (C-C and C-H), decreased as the hydrogenation temperature increased (Fig. 3(c)). The trend was more pronounced for samples treated at higher temperatures (800–900 °C). Heating at 700 °C or above can cause partial graphitization of ND in both vacuum and argon atmospheres. According to Fig. 3, hydrogen suppresses the ND graphitization at temperatures up to 900 °C. At these temperatures, hydrogen can react with sp² carbon atoms, converting them into sp³ hybridized atoms, and eventually eliminating surface carbon in the form of volatile hydrocarbons. Hence, we conclude that the heating of ND in hydrogen at temperatures up to 900 °C does not induce graphitization of ND.

B. Resistivity of hydrogenated ND

The resistivities of the H-NDs (Fig. 4) were calculated from the I-V curves. The H-ND samples treated at or below 500 °C exhibited high resistivity on the order of 10⁷ Ω cm, similar to that of UD90 before purification (1.0 × 10⁷ Ω cm) and UD90p (1.9 × 10⁷ Ω cm). On the other hand, the H-ND samples treated at 600 °C or above showed almost two orders of magnitude lower resistivity than those treated at temperatures below 500 °C or untreated NDs. Further increase in hydrogenation temperature did not result in significant changes of resistivity (Fig. 4). The relationship between the hydrogenation temperature and the sp²/sp³ carbon ratio of ND (Fig. 3(b)) indicates that the treatment at high temperature did not cause graphitization of ND. Thus, it is obvious that the decrease of resistivity is not related to surface graphitization of ND. On the other hand, ND surface hydrogenation was evidenced by FTIR and XP spectra at 600 °C and above. Thus, the decrease of resistivity should be related to the ND surface hydrogenation. It is well known that hydrogen-terminated diamond films can exhibit significant electric conductivity when in contact with water or ambient humid air due to transfer doping. This mechanism was used to explain significant two-dimensional surface conductivity of hydrogen-terminated diamond. The sharp drop in the resistivity of our ND samples after hydrogenation at 600 °C and above can also be related to the transfer doping of the hydrogenated ND surface exposed to ambient air. Hydrogenated ND can be considered as a surface-conductive ND, a material with many potential applications in electrochemistry, biomedical sensing, and nanocomposites.

C. Loss of conductivity by oxidation of H-ND

In order to further confirm that the increased electric conductivity of the H-ND is related to hydrogen termination, we measured the resistivity of H-NDs after oxidation. Figure 5 shows resistivity of the H-ND (600–900 °C) samples after oxidation in air at 200 °C and 300 °C.
heating in air at 200 and 300°C for 1 h. While the resistivity of all H-ND samples showed almost no change after heating in air at 200°C, ~50 times increased resistivities were measured for the samples after heating in air at 300°C. Figure 6 shows FTIR spectra of H-ND (600°C) before and after heating in air at 200 and 300°C. Although the spectrum of a sample treated at 200°C in air is similar to the spectrum before the treatment, the increase of C=O stretching band intensity at ca. 1720 cm⁻¹ and the decrease of CH₂ symmetric and antisymmetric stretching band intensity at around 2900 cm⁻¹ was found after the treatment at 300°C. This result indicates that the H-ND surface can be oxidized by heating in air at 300°C or above, while 200°C is not sufficient for oxygen chemisorption, which is consistent with our previous results on ND oxidation. The O/C atomic ratio of H-ND samples after heating in air was quantified by XPS (Fig. 7(a)). For all the H-ND samples prepared at 600–900°C, the O/C ratio increased only slightly after the treatment at 200°C. After the treatment at 300°C, the increase in the O/C ratio was greater than that after the treatment at 200°C. This result also confirms that the loss of electric conductivity of H-ND after heating in air is due to surface oxidation. In contrast, the $sp^2/sp^3$ ratio was almost unchanged for all the H-ND samples even after the treatment in air at 300°C (Fig. 7(b)) likely because 300°C is too low for oxidation of $sp^2$ carbon in air, which starts at temperatures above 375°C. The O/C ratio of the H-ND samples after heating in air at 300°C was around 0.04, much lower than before surface hydrogenation (0.38). Thus, the heating in air at 300°C for 1 h results only in a mild oxidation of ND surface. However, even this mild oxidation is sufficient to reduce the conductivity of ND by almost two orders of magnitude (Fig. 5).

Figure 8(a) summarizes resistivity of the ND samples treated under various conditions as a function of the O/C

![Figure 6](image6.png) FIG. 6. (a) FTIR spectra of H-ND (600°C) after oxidation in air. Before oxidation (i) and oxidized at 200 (ii) and 300°C (iii). (b) CH₂/CH₃ stretching mode region of the spectra.

![Figure 7](image7.png) FIG. 7. (a) O/C atomic ratio and (b) $sp^2/sp^3$ carbon ratio estimated by XPS analysis of H-NDs (600–900°C) after oxidation in air at 200 and 300°C.

![Figure 8](image8.png) FIG. 8. (a) Resistivity of H-NDs treated under various conditions as a function of the O/C atomic ratio measured by XPS. (b) Schematic illustration of band diagrams for H-NDs with various O/C ratios.
ratio. The resistivity shows a steep transition between low ($\sim 10^5 \, \Omega \, \text{cm}$, region I) and high ($\sim 10^7 \, \Omega \, \text{cm}$, region II) regions at a critical O/C ratio of ca. 0.033. This behavior is consistent with the concept of transfer doping. The position of the valence band maximum, which is below the Fermi level in oxidized ND, shifts gradually to higher energy with increasing density of the surface C-H groups due to the dipoles with $6^+$ charge on the H atom. However, in order for the transfer doping to occur, it is critical that the valence band maximum is above the Fermi level (redox potential derived from surface adsorbates, possibly oxygen and water in this case$^{21,36}$) (Fig. 8(b)), which can only be realized at very low O/C ratios. The O/C atomic ratio of 0.033 is less than 1/10 of that for the oxidized surface (0.38). Thus, the highly hydrogenated surface is necessary for surface conductivity, which, again, is consistent with the transfer doping mechanism.

IV. CONCLUSION

The electric conductivity of ND increased by almost 2 orders of magnitude after heat treatment in hydrogen gas at 600–900 °C. Characterization with FTIR and XPS revealed that the surface hydrogenation of ND occurred at 600 °C and higher temperatures. On the other hand, analysis of the XPS C 1s spectra showed no evidence of surface graphitization at higher temperatures. On the other hand, analysis of the XPS regions at a critical O/C ratio of $d$ dipoles with increasing density of the surface C-H groups due to the level in oxidized ND, shifts gradually to higher energy with the valence band maximum, which is below the Fermi level (redox potential derived from surface adsorbates, possibly oxygen and water in this case$^{21,36}$) (Fig. 8(b)), which can only be realized at very low O/C ratios. The O/C atomic ratio of 0.033 is less than 1/10 of that for the oxidized surface (0.38). Thus, the highly hydrogenated surface is necessary for surface conductivity, which, again, is consistent with the transfer doping mechanism.

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