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Nitrogen and hydrogen plasma treatments of multiwalled carbon nanotubes

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This article investigates plasma treatment of vertically aligned multiwall carbon nanotube (CNT) films in different plasma environments for modification of surface chemistry and morphology. The surfaces of the CNTs were functionalized with a pulsed dc plasma treatment, where the power was directly applied to the nanotube film in low pressure argon/nitrogen and argon/hydrogen backgrounds. Optical emission spectroscopy was used to detect atomic and molecular excitations in the gas mixtures as well as in pure gases in the vicinity of the CNT films. *In situ* x-ray photoelectron spectroscopy was performed on the treated samples to examine CNT surface chemistry after treatment. The analysis of CNT films after nitrogen and hydrogen treatment indicated formation of both C—N and C—H bonds, respectively. Correlations of the plasma characteristics to the surface chemistry and morphology of the CNT surfaces are discussed. © 2008 American Vacuum Society. [DOI: 10.1116/1.2917068]

I. INTRODUCTION

Carbon nanotubes (CNTs) are currently of interest in many research areas due to their extreme properties of strength, thermal conductivity, field emission, and resistance to chemical degradation. One of the challenges in actual applications of CNTs is to develop effective processes to manipulate surface morphology and chemistry in order to improve CNT performance and extend their potential range of applications. Exposure of nanotubes to reactive plasmas has been reported by several authors to be a useful treatment technique. For example, field emission from CNTs can be improved by a combination of etching and chemical doping.^{1,2} Further examples of successful plasma treatment can be found in composite processing, where the intrinsic chemical resistance of CNTs makes it difficult to effectively incorporate them into the reinforced composite materials or suspend them in liquid solvents. Nitrogen-based plasma treatments have been investigated to promote interactions between CNT sidewalls and polymer matrices.³⁻⁶

This work evaluates a pulsed dc glow discharge plasma treatment for structural and chemical modifications of vertically aligned multiwalled CNT materials. Vertically aligned multiwalled CNT films (on an oxidized silicon substrate) were used as the cathode to generate a glow discharge plasma which was powered by an asymmetric bipolar pulsed power supply. This experimental setup allowed efficient pro-

duction of reactive, monotonic neutral species from molecular gases due to the relatively low electron temperatures (compared to rf or microwave plasmas), which promoted dissociative recombination of molecular gases⁷ with no additional plasma sources or matching networks. Optical emission spectroscopy was used to detect the major species in the plasma and to determine effective gas mixtures for obtaining the desired surface properties of the CNT films. X-ray photoelectron spectroscopy (XPS) was used *in situ* and *ex situ* to analyze surface chemistry of the plasma treated CNTs.

II. EXPERIMENT

Vertically aligned multiwall CNT films were obtained from Rensselaer Polytechnic Institute.⁸ Samples were placed

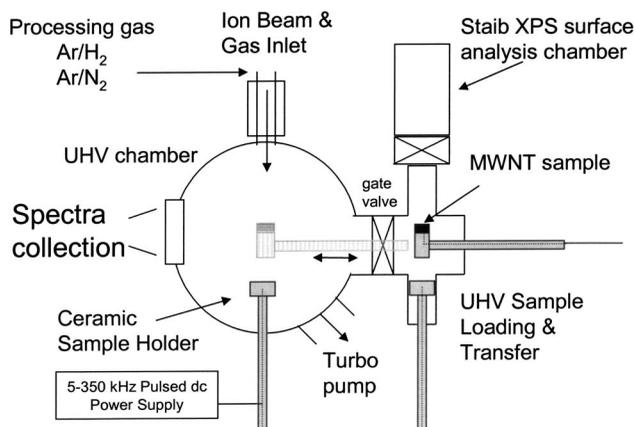
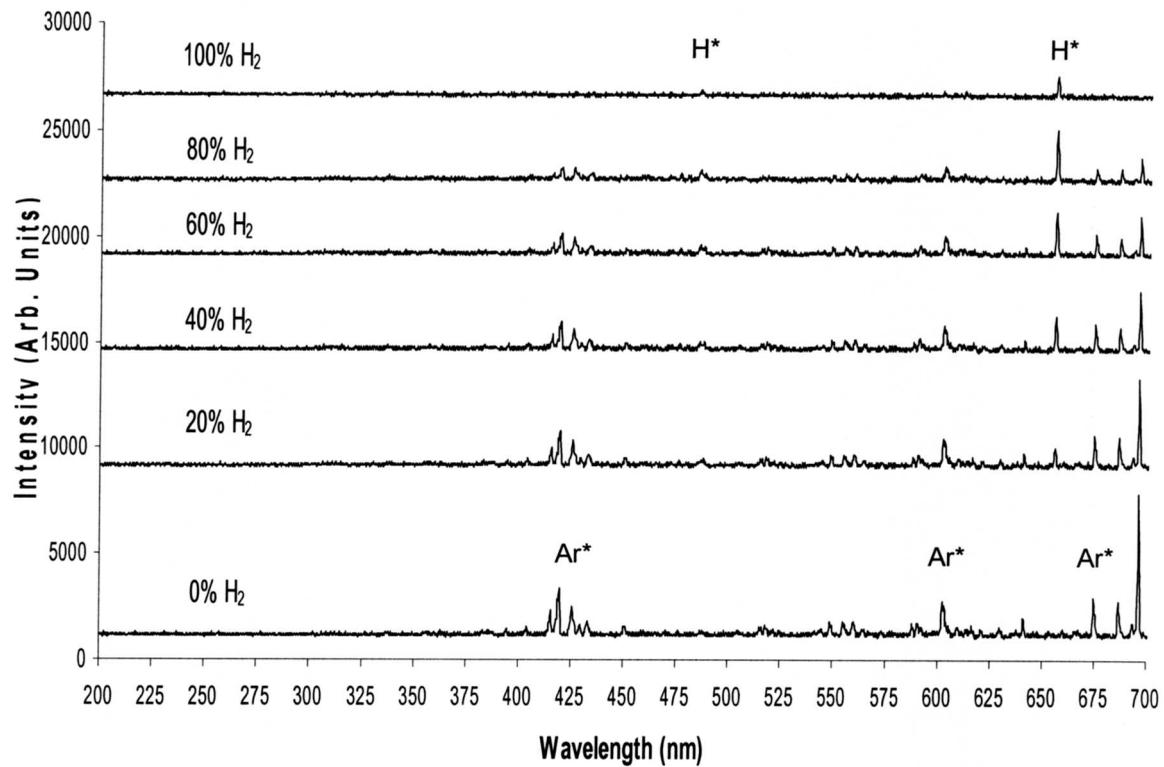
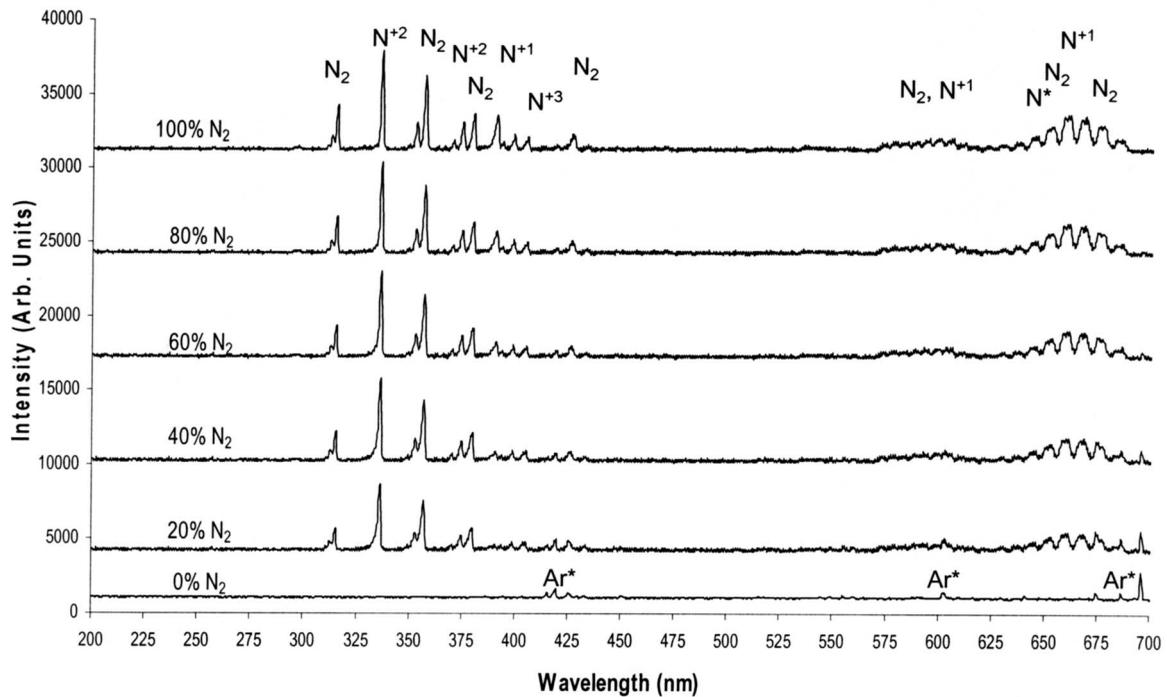


Fig. 1. UHV chamber used for plasma processing multiwall CNT films with an XPS chamber for *in situ* sample chemistry analyses.

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(a)



(b)

FIG. 2. Plasma emission spectra recorded at 4 Pa background pressures for (a) mixtures of argon and hydrogen and (b) mixtures of argon and nitrogen.

in a 20 mm thick polytetrafluoroethylene fixture to eliminate plasma generation from any surface other than that intended for treatment. The treatments were completed in the vacuum system schematically shown in Fig. 1, where the processing

chamber was evacuated to 1.3×10^{-5} Pa base pressure. Before the plasma treatment, the CNTs were sputter cleaned with a Veeco 3 cm FC ion beam source powered by an Ion Tech MPS3000 FC power supply for 5 s at a beam current of

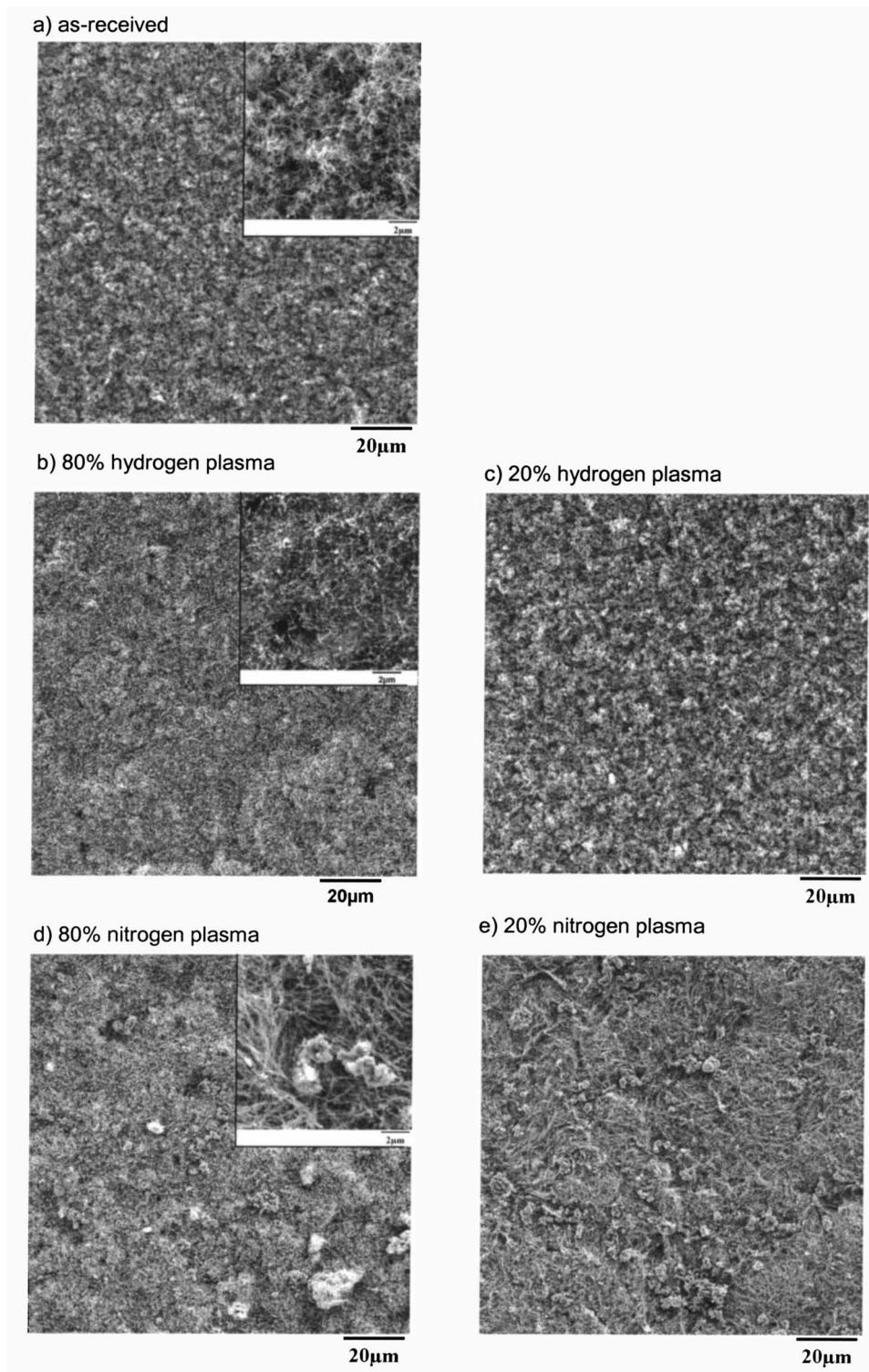


FIG. 3. SEM images for (a) as received multiwall CNT film, (b) after treatment with 80% H_2 plasma, (c) after treatment with 20% H_2 plasma, (d) after treatment with 80% N_2 plasma, and (e) after treatment with 20% N_2 plasma.

9 mA and an accelerating potential of -300 V with 4 SCCM (SCCM denotes cubic centimeter per minute at STP) of argon flowing through the ion beam source. After ion beam cleaning, the chamber was evacuated to the base pressure and refilled with a gas mixture of argon and hydrogen or argon and nitrogen. For each gas mixture, the chamber pressure was maintained at 4 Pa with a total gas flow rate of 50 SCCM, where the flow rates of reactive gas (hydrogen or

nitrogen) were set to be 0%, 20%, 40%, 60%, 80%, and 100% of the total gas flow rate. The reactive plasma treatment was accomplished using an Advanced Energy Pinnacle Plus dc pulsed power supply at a nominal -600 V, with a pulse frequency of 150 kHz, and a reverse time of $1 \mu s$. Power was directly applied to the sample, making it the primary cathode for plasma generation, while the ground for the power supply was connected to the chamber. The application

TABLE I. Detected species, identified transitions, and corresponding wavelengths in nanometers.

Species	Transition	nm
N2 (second positive)	$C^3\Pi_u-B^3\Pi_g$	307–316
N2 (second positive)	$C^3\Pi_u-B^3\Pi_g$	315.4
N III	$4P^0-4P$	336.734
N2 II	$B^2\Sigma_h^+-X^2\Sigma_g^+$	353.9
N2 II	$B^2\Sigma_h^+-X^2\Sigma_g^+$	358
N2 (second positive)	$C^3\Pi_u-B^3\Pi_g$	370–380
N IV	$1P^0-1D$	374.754
N2 (second positive)	$C^3\Pi_u-B^3\Pi_g$	380
N II	$1P-1P^0$	391.9
N II	$1P^0-1D$	399.5
N IV	$1P^0-1D$	405.776
Ar I	$2[3/2]^0-2[3/2]$	415.859
Ar I	$2[3/2]^0-2[1/2]$	419.8317
Ar I	$2[1/2]^0-2[1/2]$	425.9362
N2 (second positive)	$C^3\Pi_u-B^3\Pi_g$	427
Ar I	$2[1/2]^0-2[3/2]$	433.3581
H I	$2p^0-2D$	434.047
Ar II	$2p-2p^0$	476.4865
H I	$2p^0-2D$	486.133
N II	$1P^0-3D$	574.73
N2 (first positive)	$B^3\Pi_g-A^3\Sigma_u^+$	536–612
N II	$3P-3D^0$	592.781
N II	$3P-3D^0$	595.239
N I	$2S^0-2P$	599.943
Ar I	$2[3/2]-2[1/2]^0$	602.515
Ar I	$2[5/2]-2[7/2]^0$	603.2127
N2 (first positive)	$B^3\Pi_g-A^3\Sigma_u^+$	630–690
Ar I	$2[1/2]-2[3/2]^0$	641.6307
N III	$4P-4D^0$	646.702
H I	$2p^0-2D$	656.2852
N II	$1D-1F^0$	661.056
Ar I	$2[1/2]-2[3/2]^0$	675.2834
Ar I	$2[1/2]-2[1/2]^0$	687.1289
Ar I	$2[3/2]^0-2[1/2]$	696.5431

of the pulsed power created a reactive plasma discharge around the CNTs. Samples were exposed to the plasma for 45 s. The spectra of each plasma gas mixture were collected with an Ocean Optics HR4000CG-UV-NIR high resolution spectrometer with a 200–1100 nm range, using a fiber collection bundle coupled with a fixed position focusing lens. The spectra were collected with an integration time of 1000 ms and a 4 scan average.

Out of the combinations of gas mixtures investigated, the following five were selected for plasma treatment of CNT films: 20% and 80% hydrogen in argon, 20% and 80% nitrogen in argon, and 100% argon as a control sample. *In situ* XPS scans of the five treated samples were performed on each sample without exposure to atmosphere under ultrahigh vacuum conditions using the sample transfer arrangements shown in Fig. 1. The analyses were performed using a Staib XPS system equipped with a magnesium x-ray source. XPS scans of each sample were taken as received for the treatment, after a 5 s argon ion beam cleaning procedure, and the third scan was acquired after the 45 s reactive plasma surface treatment. From the XPS analyses, the relative peak areas were measured to obtain the CNT surface elemental compositions. *Ex situ* high resolution scans were also obtained for selected samples, after they were transferred to a Surface Science Instruments XPS, which involved sample surface exposure to laboratory air. Scanning electron microscopy (SEM) of treated CNT films was used to investigate changes in surface morphology due to exposure to the reactive plasma.

III. RESULTS AND DISCUSSION

The use of a pulsed power supply was required due to the poor electrical conductivity of the oxidized silicon substrate material on which CNT films were grown. No plasma was

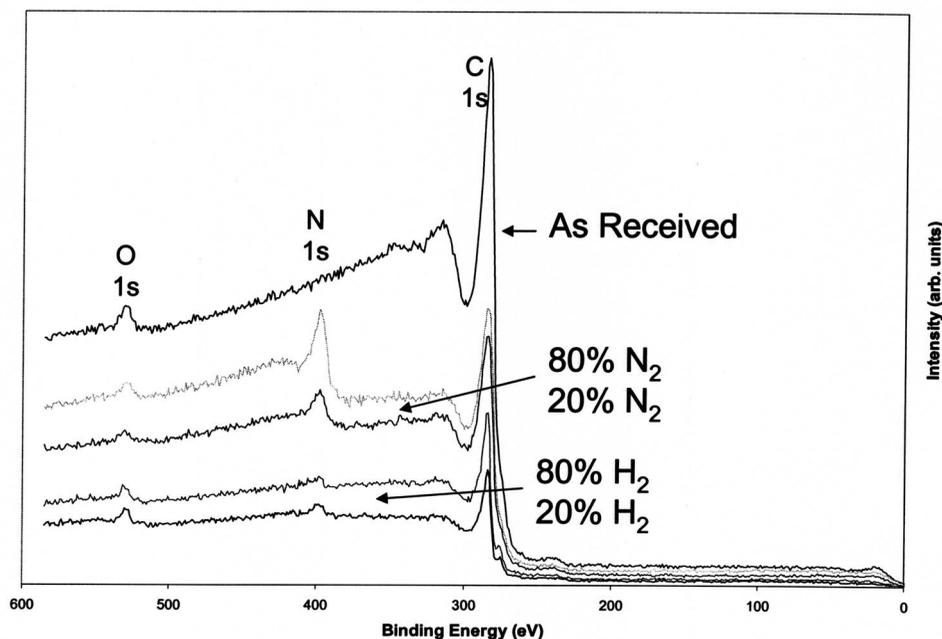


FIG. 4. XPS scans of the as received CNTs and post plasma treatment with four different environments of argon gas in combination with 80% and 20%, N₂ and H₂, all at the same 4 Pa pressure.

observed when a dc power was applied to the CNT film. The surface of the oxidized substrate charged up to the plasma floating potential, which was insufficient to sustain a discharge. Switching polarity on the microsecond time scale allows sputtering during the negative part of the cycle and neutralization of the positive charge accumulated on the target surface while it is positively biased. A frequency of 150 kHz was selected as it was the minimum required to initiate and sustain a stable glow discharge with the CNT film and substrate acting as the plasma cathode.

Optical emission spectra were collected for pulsed plasmas produced with mixtures of hydrogen and nitrogen with argon (Fig. 2). The detected transitions were for atomic species, such as excited hydrogen (H^*) at 656.3 and 486.1 nm for the hydrogen plasmas. In the 80% hydrogen plasma, both H^* peak intensities were at their maximum. The H^* emission intensities for the 100% hydrogen plasma were equivalent to the intensities from the 20% hydrogen plasma. For the cases of 20%, 40%, 60%, and 80% hydrogen, there was a monotonic increase in H^* emission and a linear decrease in excited argon (Ar^*) emissions (Fig. 2).

In the nitrogen plasmas, both monatomic and diatomic species were detected. The predominant species were excited nitrogen gas (first and second positive, N_2^*), excited monatomic nitrogen (N^*), and singly ionized monatomic nitrogen (N^+) (Fig. 2). Although the intensities of all nitrogen peaks decreased with nitrogen content, the reduction of intensity for some peaks was nonlinear, with most peaks maintaining a large fraction of their full intensities down to 20% nitrogen. The peak that appeared to be most sensitive to nitrogen partial pressure was the N^+ peak at 391 nm. It was nonexistent at 20% nitrogen but it grew much quicker than all the other peaks with increasing nitrogen gas content in the plasma, suggesting that the atomic ion formed in a multistep process which was likely dissociative recombination of molecular ions, followed by ionization of neutral atomic nitrogen. As in the hydrogen plasma, all argon peaks were Ar^* with intensity linearly increasing with the partial pressure of argon. Further details of each detected species and its corresponding transition are listed in Table I.⁹⁻¹⁵

SEM images show the morphological changes that occur from the different plasma treatments (Fig. 3). The multi-walled CNTs treated with the 80% hydrogen plasma [Fig. 3(b) and inset] showed etching of the tangled nanotubes at the surface and a similar “nanoparticle welded” structure as that reported by Yu *et al.*,¹ which was shown to reduce turn-on fields and increase emission current density in field emission tests of CNTs. This same structure was seen to a lesser degree in the 20% hydrogen plasma treated sample [Fig. 3(c)]. The sample exposed to the 80% nitrogen plasma [Fig. 3(d) and inset] showed ball-shaped structures at the ends of bundled tubes, similar to that shown by Gohel *et al.*² with a 10 min remote rf plasma treatment, which also, like the hydrogen plasma treatment, yielded similar improvements on field emission characteristics of vertically aligned, multiwalled nanotubes. The 20% nitrogen plasma treated sample also showed the same ball-shaped structures at the

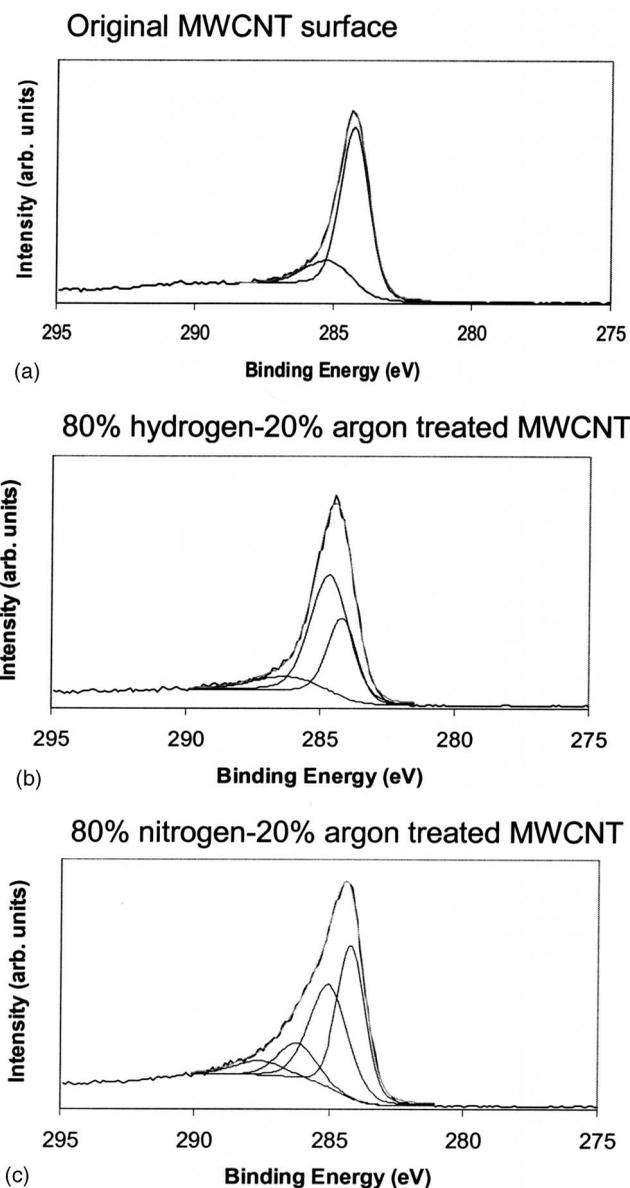


Fig. 5. Comparison of XPS C 1s bonding energies for (a) as received CNT film, (b) after treatment with 80% H_2 , and (c) after treatment with 80% N_2 .

end of the bundled tubes but the fused bundles were typically smaller than the sample exposed to the 80% nitrogen plasma [Fig. 3(e)].

XPS characterization was performed on all samples immediately after treatment without removing the samples from the vacuum chamber after processing (Fig. 4). The as received scan is included in comparison with the treated samples. For samples treated with the 80% and 20% hydrogen plasmas, the XPS analysis showed residual oxygen and nitrogen content. For the case of the 80% and 20% nitrogen treated samples, there is a strong N 1s peak present. For the 80% nitrogen treated sample, the XPS N 1s peak measurement represents 13% atomic nitrogen in the CNT sample.

High resolution XPS measurements were taken *ex situ* (after exposure to atmosphere) of selected samples (Fig. 5) to observe the features of the C 1s peak, which can be used to

indicate the nature of chemical bonding of carbon to hydrogen or nitrogen. The as received CNT sample [Fig. 5(a)] showed a symmetric peak centered about 284.5 eV, as expected for the C—C bonding. In Fig. 5(b), the sample treated in 80% hydrogen showed the broadening of the carbon peak that could be well fit with a second peak centered at 285 eV, in agreement with the reported C—H bond energy.¹⁶ The CNT film treated with 80% nitrogen demonstrated further broadening, which could be fit by adding peaks at 286.2 (C=N bonds) and 287.3 eV (C—N bonding).¹⁶ It was difficult to definitively determine whether the shifts are due to C—N or C—O species; however, survey scans immediately taken after processing (Fig. 4) and *ex situ* (not shown) reveal that the oxygen content was negligible. Similar alterations in the chemistry of nitrogen plasma-treated nanotubes were observed by others and were reported to improve adhesion between nanotubes and polymer matrices.⁵

Thus, plasma treatment of vertically aligned nanotube films with a midfrequency pulsed dc power supply as a plasma cathode in molecular gases is an effective way to alter the structure and surface chemistry of the CNTs. This technique can be used for CNT surface functionalization that can be tailored to different applications, e.g., the process described in this article was used for controlling tribological properties of multiwall CNTs.¹⁷ The results of this treatment are consistent with that previously reported by the authors using more complex techniques,^{1,4–6} and pulsed plasma treatment offers a technologically simple and controllable process for CNT surface modifications.

IV. CONCLUSIONS

Vertically aligned multiwall CNTs on an oxidized silicon wafer were treated in both hydrogen and nitrogen-based plasmas. Optical emission spectroscopy revealed that the resulting glow discharge plasma effectively produced reactive atomic ions from molecular hydrogen and nitrogen processing gases. XPS and SEM were used to show that exposure of the CNT surface to these reactive atomic species in a bipolar

pulsed discharge plasma resulted in the incorporation of hydrogen and nitrogen into the CNT structure. It was found that this process yielded surface chemistries and morphologies similar to those produced in rf and microwave plasma treatments. The pulsed dc glow discharge plasma modification of CNTs can be a simple means of treating CNT materials for surface functionalization tailored to their applications.

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