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Micro glow plasma for localized nanostructural modification of carbon nanotube forest

Mirza Saquib us Sarwar, Zhiming Xiao, Tanveer Saleh, Alireza Nojeh, and Kenichi Takahata
University of British Columbia, Vancouver, British Columbia V6T 1Z4, Canada

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This paper reports the localized selective treatment of vertically aligned carbon nanotubes, or CNT forests, for radial size modification of the nanotubes through a micro-scale glow plasma established on the material. An atmospheric-pressure DC glow plasma is shown to be stably sustained on the surface of the CNT forest in argon using micromachined tungsten electrodes with diameters down to 100 μm. Experiments reveal thinning or thickening of the nanotubes under the micro glow depending on the process conditions including discharge current and process time. These thinning and thickening effects in the treated nanotubes are measured to be up to ~30% and ~300% in their diameter, respectively, under the tested conditions. The elemental and Raman analyses suggest that the treated region of the CNT forest is pure carbon and maintains a degree of crystallinity. The local plasma treatment process investigated may allow modification of material characteristics in different domains for targeted regions or patterns, potentially aiding custom design of micro-electro-mechanical systems and other emerging devices enabled by the CNT forest. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4961629]

Vertically aligned carbon nanotubes, so called CNT forests, are considered as a functional bulk material that are promising for micro-electro-mechanical systems (MEMS) and many other application areas owing to their unique electrical, mechanical, thermal, and other properties.[1–4] CNT forests are typically grown by a chemical vapor deposition (CVD) process, in which the nanotubes are self-aligned due to crowding at the beginning of their growth.[5] This attracting material may support a broad range of potential applications, including field-emission sources,[6] sensors,[7,8] electrical interconnects,[9] heat sinks,[10] biomimetic adhesives,[11] and scanning probes.[12] In order to realize these applications, controlled functionalization is desirable to improve certain characteristics. This includes an ability to modify the radial dimension of multi-walled carbon nanotubes (MWCNTs) and control their particular physical properties such as mechanical flexibility, electrical and thermal conductivities, and optical characteristics. The functionalization of CNT forests has been approached via dry processing based on the use of glow plasma because wet processing causes collapsing of the nanotubes due to capillary effects upon drying,[13] and a variety of dry functionalization techniques have been reported.[14] An inherent characteristic of dry plasma based processes is that they lead to the degradation of the nanotubes due to the high energy particles bombarding the nanotubes and breaking the carbon-carbon bonds to generate active sites for coupling of functional groups present in the plasma; with larger energy, sputtering can occur, leading to substantial breaking and destroying of the nanotubes.[15] These, however, in turn suggest that controlled plasma processing could be used to modify the characteristics of the CNT forest surface associated with the diameter of the nanotubes, thus providing an additional mode for tuning characteristic parameters. For the dry process approach, most of the studies have been conducted through exposing the entire CNT forest or its substrate to a glow plasma. Localized functionalization of the CNT forest is an attractive and potentially powerful means to modify certain characteristics at targeted locations of the material and will vastly expand design flexibility for the application areas noted earlier. This is, however, challenging because of the difficulty in establishing a masking layer over the material as the surface is essentially a collection of the tips of the nanotubes. Furthermore, this type of processing is typically performed in a vacuum environment in order to sustain a stable plasma in a diode set-up with large planar electrodes, inherently posing issues in process efficiency and cost.

This paper reports the generation of a highly confined micro-scale glow plasma directly on the CNT forest using a micromachined electrode, in an inert gas at atmospheric pressure, enabling structural and surface modifications only at a desired region of the forest without the need for a complex vacuum system for the process. Past studies used arc or spark discharge with high discharge current densities for post-growth localized processing of CNT forests in dry ambient, with a focus on micromachining of the material, i.e., arbitrary height modification for the CNTs in the forest.[16,17] The radial modification of MWCNTs via the truncation of their outer walls, demonstrated by passing a current through the nanotubes, has been reported to involve different breakdown mechanisms.[18,19] One proposed mechanism was the removal of carbon by heat-induced oxidation when the environment contained oxygen,[19] while the phenomenon was also hypothesized that CNTs conduct ballistically and the energy to break carbon bonds originates from highly localized dissipation at defect scattering sites.[18] While these studies only showed the reduction of the diameter, the current method based on micro glow enables both the reduction and the enlargement of the diameter, offering two degrees of freedom in the radial adjustment, without removing/shortening the CNTs unlike the arc discharge techniques. This ability could offer broader applications of the CNT forest

through tailored nanotube characteristics in terms of electrical, thermal, and mechanical properties. The local micro glow process can be easily incorporated in the numerical control system for dry micromachining process based on the micro arc discharge,[16,17] so that a CNT forest sample could be processed with both methods for full geometrical modification of the CNTs along both their longitudinal and radial directions with high precision.

The MWCNT forest samples used in this study are grown on a highly doped silicon wafer that has an evaporated catalytic layer of iron (2 nm) and alumina (10 nm) using atmospheric CVD; details of the growth process can be found in a previous report.[13] A micro-scale DC glow plasma is generated between a cylindrically shaped tungsten microelectrode and the top surface of a forest with a gap separating the two. A schematic of the set-up is shown in Fig. 1. The relative position of the electrode's tip with respect to the forest sample is controlled using a high-precision three-axis stage (with a positioning resolution of 100 nm in all axes). The forest sample is held on the XY stage and connected to the discharge circuit through its silicon substrate using a conductive carbon tape. A DC voltage ranging from 200 V to 400 V is applied between them, through a series connected resistor (690 kΩ) for discharge current regulation, so that the microelectrode serves as the cathode to generate and sustain a glow plasma in this point-to-plane diode setting. The microelectrode is shaped using a commercial micro-electro-discharge machine (EM203, SmalTec International, IL, USA) to have a diameter in the range of 100–300 μm. The discharge is generated in argon inside an enclosure to maintain a consistent gas environment. In one experiment, oxygen is mixed with argon aiming to evaluate the effects of oxidation-related breakdown of the MWCNT[20] and compare with the results of processing using a solely physical mechanism with pure argon. To ensure the delivery of a homogenized gas mixture with a target oxygen concentration to the processing area, argon and oxygen are first fed to a buffer chamber with adjusted flow rates (oxygen concentration is monitored using an oxygen sensor (VN202, Vandagraph Co., UK)) prior to the process chamber.

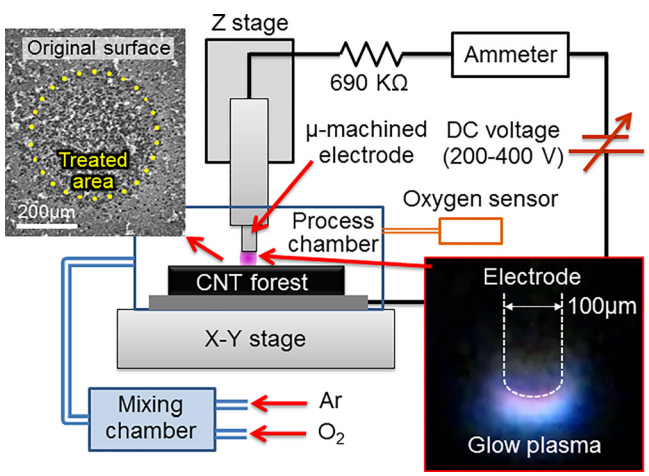

FIG. 1. Schematic of micro glow experimental set-up. The inset optical image (right) shows a DC glow plasma created on CNT forest using a 100-μm-diameter tungsten electrode. The inset SEM image (left) shows a local region processed (using a different electrode) on the original forest surface.

A glow discharge is triggered by feeding the electrode towards the CNT forest surface in a controlled manner while a DC voltage is applied. Upon reaching the necessary electric field strength (approximately in the order of 1 MV m^{-1} for argon at atmospheric pressure[21]), the gas is ionized to cause avalanche breakdown leading to plasma generation that conducts a current. As conduction occurs, a glow (with bluish optical emissions) is established under the electrode tip in a confined form (Fig. 1). Current readings range from 100 μA to 400 μA with applied voltages from 200 V to 400 V. The gap size between the forest and the electrode necessary to trigger and sustain the glow plasma is typically a few tens of μm for the set-up described, approximately translating to an electric field range of 3–10 MV·m^{-1}. This is consistent with the level of theoretical breakdown strength. The smallest diameter of the electrode that could sustain a stable glow was observed to be 100 μm in the used set-up. It is worth noting that the use of CNT forest as the anode aids in attaining a stable micro glow; the opposite polarity tends to cause aggressive discharge, most likely due to a field enhancement effect brought about by the CNTs, making the process unstable. It was verified that once the micro glow was established, it could be laterally manipulated over the forest surface using the XY stage, representing an essential ability to perform local treatment of the forest with an arbitrary pattern.

Micro plasma processing was performed on an identical CNT forest sample in argon ambient, with varying oxygen concentrations from zero up to 4.2%, each for a constant time of 5 s. The discharge current was maintained at 100 μA. The treated regions of the forest surface were analyzed using a scanning electron microscope (SEM, Hitachi S3000N; Figs. 2(a)–2(d)). The changes in the radial size of the processed nanotubes were visible. To quantify this observation, SEM images were used to determine the average diameter of the CNTs by measuring the diameters of randomly selected nanotubes ($n = 30$) in each image. The results illustrated in Fig. 2(e) clearly show a reduction in the nanotube diameter in the pure argon ambient, exhibiting ~30% reduction from the average diameter of the original (unprocessed) nanotubes. In the past reports showing the breakdown of outer walls of MWCNTs,[18,19] the level of the current flowing through the single MWCNT was around 170–200 μA. In our micro glow setting, however, the current passing through each MWCNT can be estimated to be in the order of 10 pA, assuming that the density of the nanotubes in the forest is ~10^{11} cm^{-2},[22] and that the electron flux is confined within the diameter of the tungsten electrode tip (100 μm). The outer wall breakdown of the MWCNT reported for the arc discharge process[23] involved an arc current of 5 μA passing through the ~10-μm tip of the electrode; although the CNT forest density involved in this particular report is unknown, assuming the same conditions as our case (forest density of 10^{11} cm^{-2}, and the arc current passed through a forest area equivalent to that of the electrode tip), the current flowing through an individual CNT in this case is estimated be in the same order as this micro glow process.

Fig. 2(e) also indicates a consistent trend in the diameters of treated CNTs with oxygen concentration, i.e., incorporating more oxygen in the argon environment led to a lower reduction in diameter. This outcome appears to be

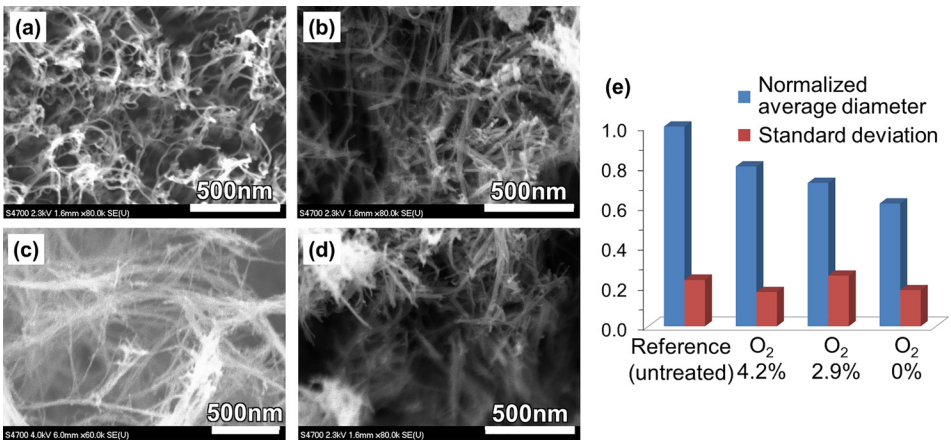

FIG. 2. SEM images showing the thinning effect observed in a CNT forest before and after localized plasma processing for 5 s in argon with varying oxygen concentrations: (a) Untreated CNTs, and treated CNTs with oxygen concentration of (b) 0%, (c) 2.9%, and (d) 4.2%. (e) Average diameters of CNTs (analyzed from SEM images and normalized) before and after the process.

contrary to what may be expected from the past studies that reported current-induced outer wall breakdown with potential oxidation effects.[19] A phenomenon observed and potentially related to this outcome was that the micro glow discharge became unstable with addition of oxygen; the discharge could be extinguished faster with higher concentration of oxygen introduced. It was reported that the mixture of oxygen into atmospheric glow plasma in argon caused more consumption of free electrons in the plasma and thus made it more resistive,[24] which may explain the resultant instability in sustaining the micro glow. Although there might have been oxidation effects in the diameter reduction with the mixture of oxygen, the glow instability could have been the primary factor that led to the observed trend in diameter reduction with oxygen concentration.

Further characterization was performed by varying the discharge current (up to 400 μA) while sustaining a micro glow for durations up to 60 s under a pure argon environment. SEM analysis of the top surface of the processed forest showed that for higher discharge currents, granular structures began to appear shortly (within ~5 s) after the ignition of micro glow. Being exposed long enough (e.g., 10 s) to a current as low as 100 μA, the processed surface showed a similar morphology. These results insinuate that the morphology change observed was a function of energy rather than current. Compared with the untreated surface (Fig. 3(a)), the CNTs became thinner when exposed to the glow with a process time and current of 10 s and 100 μA, respectively, consistent with the result from the previous experiment. With a prolonged discharge and/or with a high discharge current, the CNTs were observed to form thicker structures; increasing the current clearly enhanced this thickening phenomenon in a consistent manner as illustrated in Figs. 3(b)–3(e). (These thickened structures are analyzed later.) As can be seen from these images, with current increase, the tips of the nanotubes formed spherical shapes, which apparently constituted the granular-like topology on the forest surface. A similar thickening phenomenon was reported in micromachining of CNT forests based on pulsed arc discharge generated using a similar tungsten microelectrode.[16] Thickened CNT structures coalesced together to grow further as the process was extended (Fig. 3(f)). The average diameters of the processed nanotubes for different currents shown in Fig. 3(h), quantified in the same manner as described earlier, clearly verifies the dependence of the thickening effect on the discharge current. As displayed, a substantial increase was observed in the transition of current increase from 100 μA to 176 μA, eventually reaching a ~3× average diameter with a 3.2× raise of the current. The current density involved in this experiment approximately ranged 10–40 kA m^{-2} (calculated using the electrode area). Bundling of CNTs was reported to form needle-like structures after dry etching of the forest using a typical macro-scale plasma generated in an argon-oxygen mixed ambient[25]—it is worth noting that although that particular study used a range of discharge current (13–26 kA m^{-2}) similar to the present case, the resultant nanotube structures and surface topologies appeared to be largely dissimilar (e.g., spherical tips vs. needle-like tips).

The treated regions were also analyzed using energy-dispersive x-ray spectroscopy (EDX, available in the same

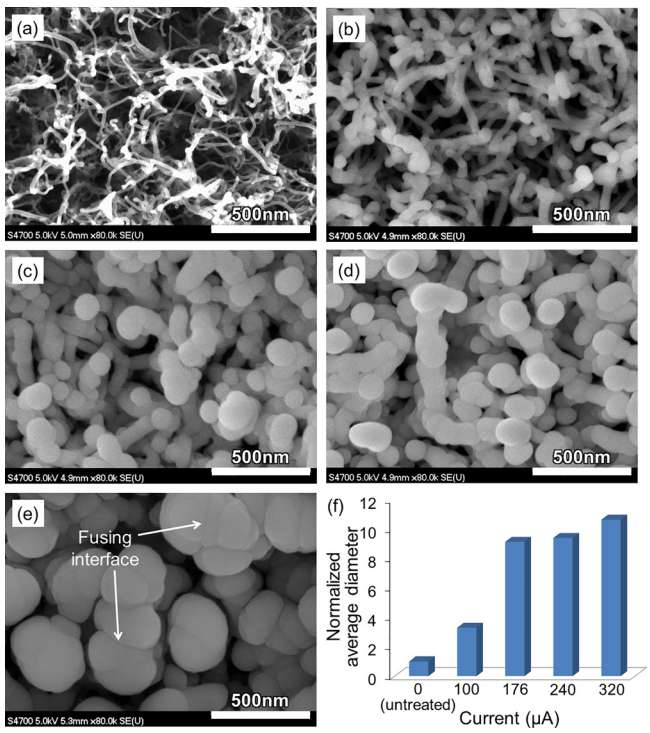

FIG. 3. SEM images showing the thickening and coalescing effect observed in a CNT forest before and after localized plasma processing for 60 s in pure argon with varying discharge currents: (a) Untreated CNTs and treated CNTs with the current of (b) 100 μA, (c) 176 μA, and (d) 320 μA. (e) A close-up of the CNT tips (treaetd with 320 μA) showing coalescing of their structutres. (f) Average diameters of CNTs (analyzed from SEM images and normalized) before and after the process.

SEM system used). It was observed as shown in Fig. 4(a) that carbon content decreased with increase in the discharge current, accompanied by an increase in the signal of silicon. The signal source of silicon was the substrate on which the CNT forest was grown, i.e., the incident beam penetrated through the forest and reached the substrate surface to produce its signal being captured by the EDX detector.[26] The K-ratio values of carbon decreased by 21%–22% with a 2× increase in the discharge current while those of silicon increased by 22%–24% both in consistent manners. A possible explanation of this result is that the CNTs were thickened by bundling together, creating more open spaces for the incident beam to reach the substrate and produce more signals of silicon compared with those of carbon. The EDX analysis also showed that the levels of tungsten, the electrode material, or any other contaminant (except for a slight amount of oxygen that might have been trapped within the forest) were negligible, suggesting that the structures were carbon indeed and that the electrode wear was minimal.

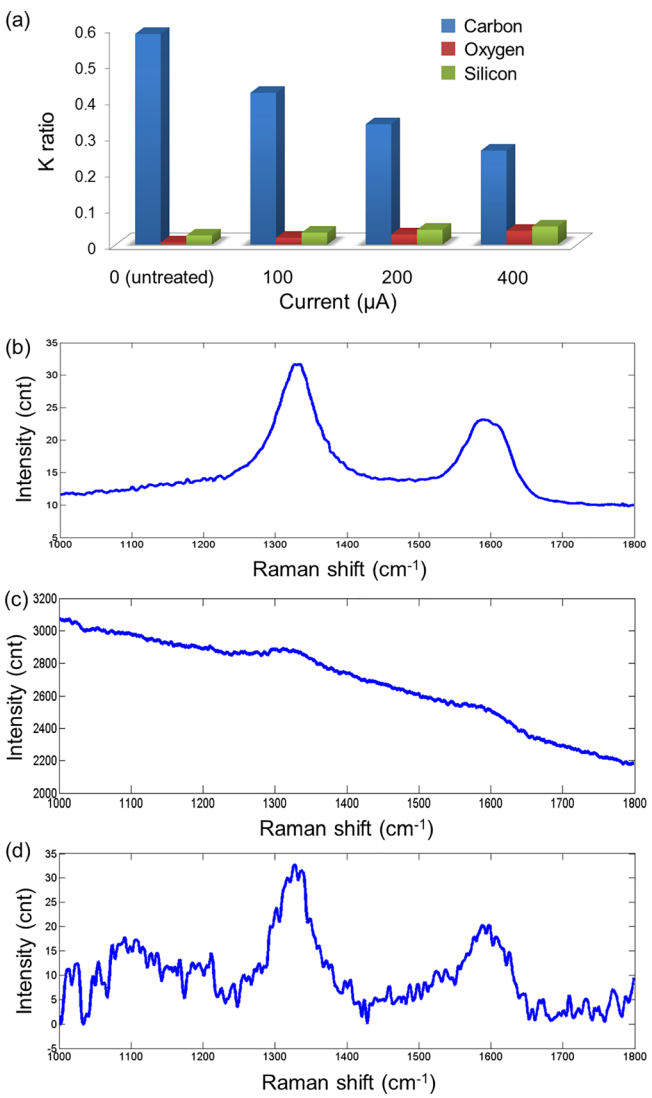

FIG. 4. (a) EDX analysis of a CNT forest surface processed with the micro glow plasma, and results from Raman spectroscopy of the forest for (b) untreated surface (without background correction), (c) treated surface without background correction, and (d) treated surface with background correction.

Raman spectroscopy was used to analyze a treated region (with 200 μA for 5 s) with the thickened structures in comparison with untreated CNTs in the same forest sample. The reference region (Fig. 4(b)) showed two distinct peaks corresponding to the D- and G-bands ($I_D = 1342\,\mathrm{cm}^{-1}$ and $I_G = 1580\,\mathrm{cm}^{-1}$, consistent with previously reported results[16]). The treated region, however, showed massively more background noise (Fig. 4(c)) compared with the reference region. Applying a background correction to the raw spectrum (two-degree polynomial fitting and subtraction from the raw data) provided a substantially more interpretable signal (Fig. 4(d)), with the peaks, I_D and I_G, at nearly the same wavenumbers as the reference region. This insinuates the existence of similar inelastic scattering as that of the original CNTs, but enveloped under a substantial background usually generated by the existence of fluorescent material.[27] The ratio I_D/I_G in both the cases appears to be ~1.62, indicating a similar level of disorder in the CNT structures before and after the discharge process. One possible conclusion regarding the thickened structures could be either that these structures themselves are the fluorescent entity, or that they have contaminants that are fluorescent. In either case, a transformation of the CNTs appears to have been present. The EDX results support that there were nearly no contaminants, which backs the hypothesis that the thickened structures are derivatives of CNTs that have less organized molecular arrangement. One possible condition is that there is still a CNT core, surrounded by amorphous coalesced structures, or that the entire structure is coalesced with some retaining fragments of CNT (that appeared in the Raman after background correction in Fig. 4(d)). The produced amorphous material could be continuously deposited on the CNTs in the plasma as there was no oxygen, an agent known to remove amorphous carbon.[25] To verify this hypothesis, the CNT forest was treated over different durations of time and the Raman results were analyzed. A gradual decay of the distinct peaks in the reference CNT surface to a degraded spectrum for one exposed for 1 s was observed. In the case of the region exposed for 5 s, two slight bumps were barely seen. After implementing the background correction algorithm, the characteristic peaks were again visible, which demonstrates the presence of CNTs.

This study has demonstrated that a micro-scale glow plasma can be generated and sustained on the MWCNT forest to locally treat the nanotubes in the material at atmospheric pressure. Processing in argon ambient, with or without oxygen, resulted in the reduction of the CNTs diameters by possible breakdown of their outer walls. A theoretical estimation did not support the current induced breakdown reported in the past, implying that it could be related to physical bombardment in the plasma. Thickening of CNT structures occurred with higher discharge currents and/or longer process times. Through x-ray and Raman spectroscopy, these thickened structures appeared to be derivatives of the CNTs, possibly amorphous carbon with a nanotube core. The processed CNTs were also shown to exhibit almost no contamination by the material of the microelectode, tungsten. Future work will encompass optimization of micro glow conditions and further analyses of treated nanotubes (via, e.g., transmission electron microscopy and x-ray diffraction) as well as process

characteristics including spatial resolution and scaling effects with electrode dimensions.

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