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Patterning flexible single-walled carbon nanotube thin films by an ozone gas exposure method

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ABSTRACT

Patterning is an essential and important process for the future use of single-walled carbon nanotube (SWCNT) thin films (TFs) in electronic devices. Different from traditional Si based electronic materials, SWCNTs can be easily etched when exposed to an oxidative atmosphere. Here we propose a gas exposure method to pattern SWCNT TFs on flexible polymeric substrates, without using vacuum and high temperature treatment. By simply exposing them to ozone for 3 min, a high quality SWCNT TF (35–40 nm in thickness) pattern is obtained on a poly (ethylene terephthalate) substrate. It is found that the ozone can chemisorb on, functionalize and etch SWCNTs and then destroy the electrically conductive network of SWCNT TFs, which causes a fast resistance increase and achieves efficient SWCNT TF patterns. The proposed patterning method has the advantages of high efficiency, low cost and scale-up ability, and more importantly, it is suitable for assembling flexible electronic devices, indicating prospects for the low-cost and large-scale manufacture of such items.

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1. Introduction

A single-walled carbon nanotube (SWCNT) thin film (TF) shows good electrical properties [1,2], good flexibility and high transparency [3,4]. Therefore, it is considered to be an ideal material for future electronics, especially, flexible and transparent electronics [3–7]. To assemble TFs into devices, including organic light-emitting diodes [8], sensors [9], touch panels [10], transistors and large area integrated circuits [11,12], patterning is a critical process. However, due to the chemical inertness of SWCNTs, wet etching is not suitable for patterning SWCNT TFs. In general, the patterning methods of SWCNT TFs are “borrowed” from silicon-based electronics manufacturing methods: photolithography and subsequent oxygen plasma etching [13,14]. These processes can be used in obtaining SWCNT TF patterns, however, the oxygen plasma equipment required is very expensive and the etching process is complex and time-consuming [15].

Distinct from silicon and silicon-based electronic materials, SWCNTs are easy to be etched in air or other oxidizing gases including a mixture of Ar, O₂ and H₂O, and mixture of H₂S and O₂ at ambient pressure [16]. Therefore, this offers a potential way to pattern SWCNT films using a gas phase etching method instead of a vacuum oxygen plasma [17]. However, due to the high chemical stability of SWCNTs, oxidizing temperatures are normally higher than 300 °C. This is not applicable for patterning flexible SWCNT TFs supported by polymeric substrates.

Unlike other gas phase oxidants, ozone can etch SWCNTs at a much lower temperature that can be tolerated by plastic substrates [18–20]. This is because ozone molecules not only attack the caps and defective sites of SWCNTs, but also functionalize non-defective areas in sidewalls through chemisorption according to the Criegee's mechanism [18,21]. In the process, ozone molecules chemisorb on SWCNTs with a relatively low activation energy, then through a cycloaddition

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reaction, form a primary ozonide which is unstable and subsequently forms epoxide or carbonyl functional groups, and finally evolves CO and CO₂ gas [18,21].

Inspired by the above results, we propose a simple gas exposure patterning method combining photolithography with subsequent ozone gas exposure etching (OGEE) to obtain patterned SWCNT TFs on a poly(ethylene terephthalate) (PET) substrate. After photolithography, SWCNT TF patterns can be obtained by simply exposing the film to ozone gas for several minutes at ambient pressure and a temperature below 150 °C. For a SWCNT TF with a thickness of 35–40 nm, after 3 min ozone treatment at 135 °C, the undesired part exposed to ozone is damaged and shows a 7 orders of magnitude increase in electrical resistance. The desired part of the SWCNT TFs, protected by a photoresist (PR), is retained to form the pattern on the flexible PET substrate. This method is not only time-efficient, low cost and easy to be scaled-up, but also a more practical choice for patterning SWCNT films on polymeric substrates for the assembly of further flexible devices.

Furthermore, previous reports usually emphasized the effect of ozone treatment on the electrical transport behavior of a single SWCNT [18,21]. Here, we studied the interaction between ozone and a SWCNT network, such as is present in most SWCNT devices (aside from single and parallel aligned SWCNT devices), and shows an electrical transport mechanism different from isolated SWCNTs due to the huge number of complicated tube–tube connections. The morphology evolution of SWCNT network and structure degradation of SWCNT TFs exposed to ozone gas shows that ozone can chemisorb on, functionalize, and etch SWCNTs, then destroy the electrical transport of the SWCNT network to a point far below the percolation threshold, which causes a rapid resistance increase and achieves efficient SWCNT TF patterns.

2. Experimental

2.1. Fabrication of SWCNT TFs

The SWCNTs used were synthesized by a floating chemical vapor deposition method in our lab, and the as-prepared sample was purified in air at 350 °C for 10 h and subsequently refluxed in hydrochloric acid for 10 h to remove carbon byproducts and metal catalysts.

SWCNT TFs were fabricated by a filtration-transfer method. Briefly, purified SWCNTs were firstly tip sonicated for 1 h in deionized water with a concentration of 0.1 mgml⁻¹ with the assistance of 0.5 wt.% sodium dodecyl sulfate (Sigma-Aldrich). The solution was subsequently centrifuged at 12,000 rpm for 10 min, and the supernatant obtained was diluted. Then the solution was vacuum filtered through a cellulose acetate membrane. After that, a poly(dimethyl siloxane) membrane was used as an intermediate to transfer the SWCNT TF from the cellulose acetate membrane, and place the TF onto a PET substrate whose surface energy was decreased by oxygen plasma treatment for 30 s.

2.2. Patterning of SWCNT TFs

Fig. 1a and S1 shows the schematic of a SWCNT TF patterned by photolithography and subsequent OGEE. First, a positive PR

(AZ1813) was spin-coated at 5000 rpm for 30 s onto the SWCNT TF supported by a PET substrate, followed by exposing the film to UV light through a designed photo mask at an energy density of 2.4 mJcm⁻², and developing in a 0.6 wt.% NaOH solution to remove the exposed PR [22].

The TF patterned with PR was placed on a hot plate at 135 °C, and exposed to ozone which was produced by an ozone generator (Qingdao Guolin Industry Co., Ltd.) for a short period (from 0.5 to 10 min to monitor the evolution of SWCNTs and their network). The ozone concentration was ~70%. Then the TF was rinsed in acetone to remove PR. As a result, the SWCNTs protected by PR remained intact, and the SWCNTs exposed to ozone were functionalized and etched, which enables the formation of a pattern on SWCNT TFs.

2.3. Characterization of SWCNT patterns

The patterns were observed by an optical microscope (Nikon LV100D). The sheet resistance of the pristine TFs was measured by a four-point probe meter (4-probe tech.). The thickness of the SWCNT films deposited on a Si substrate was measured by an atomic force microscope (AFM; Multimode NanoScope IIIa, Veeco, operated in the tapping mode). The transparency at 550 nm wavelength was measured by an UV–vis–NIR spectrophotometer (Cary 5000) and the electrical resistance change was monitored in situ with a 2-probe configuration by a Keithley 2400 sourcemeter. The morphology, structure and elemental composition of SWCNT TFs with different ozone exposure times were characterized by a scanning electron microscope (SEM; Nova Nano SEM 463), a 632.8 nm laser Raman spectroscopy with a JY HR800 under ambient conditions and a X-ray photoelectron spectroscopy (XPS) probe (ESCALAB 250) using focused monochromatized Al K α radiation (1486.6 eV), respectively. The SEM, Raman and XPS characterizations were made on Si substrates. The Infrared ray (IR) image was taken using an IR camera (Fluke ti32) for a patterned SWCNT TF with 3 min ozone treatment. To characterize the effectiveness of the patterns, the electroluminescent (EL) device was fabricated, a mixture of Cu-doped ZnS and epoxy resin as a phosphor layer was spin-coated onto a SWCNT pattern, which was treated in ozone for 5 min. A mixture of BaTiO₃ and epoxy resin was spin-coated on top of a ZnS layer as an insulating layer. An aluminum foil was placed on the top of the BaTiO₃ layer as an electrode [22].

3. Results and discussion

The SWCNT TFs used were fabricated by a filtration-transfer method, and have a sheet resistance of 200 Ω sq⁻¹ with a thickness of 35–40 nm (the transmittance is 75% at 550 nm wavelength). They were used without any doping treatment, which excludes any possible influence on the structure and electrical properties of SWCNTs caused by other chemicals. Then, the SWCNT TFs were patterned by photolithography and subsequent OGEE at 135 °C in ambient atmosphere as shown in Fig. 1a and S1. During patterning, the SWCNTs underneath the PR are protected from ozone etching, while the rest of SWCNTs are damaged. Fig. 1b–e show the patterns

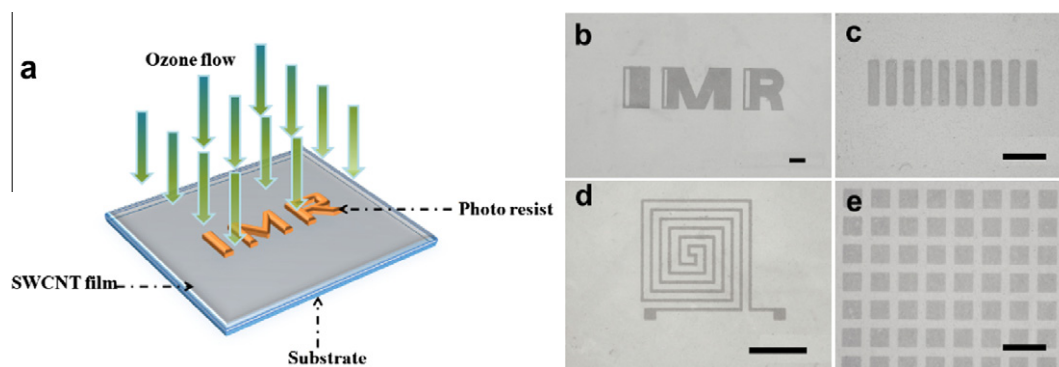


Fig. 1 – (a) Schematic of the SWCNT TF patterning process by OGEE at ambient pressure and (b–e) optical images of the obtained SWCNT TF patterns on PET substrates. (b) An “IMR” pattern; (c) A line pattern array with a 40 μm width; (d) A complicated line pattern with a 10 μm width; (e) A square array with a 50 μm side length. The scale bar represents 100 μm .

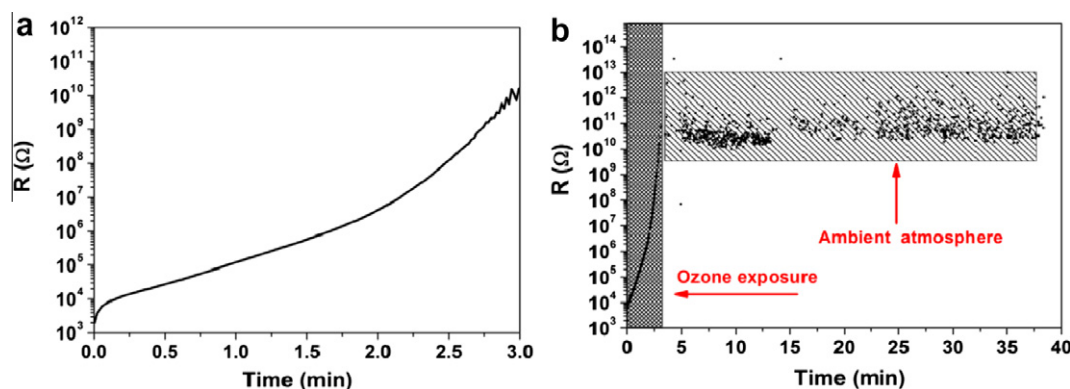


Fig. 2 – (a) Time dependence of the electrical resistance of a SWCNT TF treated with ozone. (b) The resistance of the etched SWCNT TF undergoing heat treatment at 135 $^{\circ}\text{C}$ in air for ~ 35 min.

obtained by the OGEE treatment. It can be seen that the areas treated by ozone are more transparent than that protected by the PR. Clear and uniform patterns shows the high quality and effectiveness of the method.

To further identify the effectiveness of OGEE for SWCNT TFs, the electrical resistance evolution of a SWCNT TF strip (3.5 \times 30 mm) was measured during OGEE treatment. As shown in Fig. 2a, the original electrical resistance of the TF strip was 2 k Ω , and it increased quickly when the film was exposed to ozone. Interestingly, it shows a nonlinear three-stage increase with exposure time. The resistance showed a sharp increase during the first few seconds of exposure, then an obvious slower change for the following 2 min and an accelerated increase again after 2.5 min until saturation occurred at around 10 G Ω (reaching the limit of our measuring system). This indicates a good insulating state of the ozone-treated areas and effective etching of the SWCNT TF. To evaluate the stability of the insulating state, the etched SWCNT TF strip was kept at 135 $^{\circ}\text{C}$ in air for ~ 35 min, with its resistance was monitored. As shown in Fig. 2b, the electrical resistance remained at a level of 10 G Ω and was stable for as long as a month in air at room temperature. Therefore, a stable TF pattern can be obtained by a 3-min OGEE treatment. K.N. Han et al. reported the patterning of SWCNT TFs by a capacitively coupled oxygen plasma [13]. In their work, the sheet

resistance was increased from 400 to 10⁶ Ωsq^{-1} after 4 min treatment. In comparison, our results showed a 7 orders of magnitude increase in electrical resistance from 2000 to 10¹⁰ Ω after 3 min treatment, which is much better and takes less time and uses simpler equipment.

Based on the above results, our OGEE method for patterning SWCNT TFs shows the following advantages: (i) Time-efficiency. Only several minutes are enough to etch a pattern on a TF despite the need for photolithography. (ii) Low cost. The process is conducted at ambient pressure and low temperature, no vacuum and related equipment is required. (iii) Easy scale-up. Ozone is a commercial oxidation agent, and the patterning process is very simple. (iv) Practicality. It is a more practical choice for patterning SWCNT films on polymeric substrates for the further assembly of flexible devices. Ozone is an oxidant that can selectively etch SWCNTs but has little effect on inert polymer substrates.

To understand the patterning mechanism of SWCNT TFs by OGEE, we investigated the morphology evolution of the SWCNT network and the structure degradation of SWCNTs as a function of ozone exposure time. As shown in Fig. 3, the original SWCNT TF is a clean and uniform network of SWCNTs (Fig. 3a), and no visible change in the network can be observed even after being exposed to ozone for 0.5 min (Fig. 3b). After exposure for 1 min, amorphous carbon

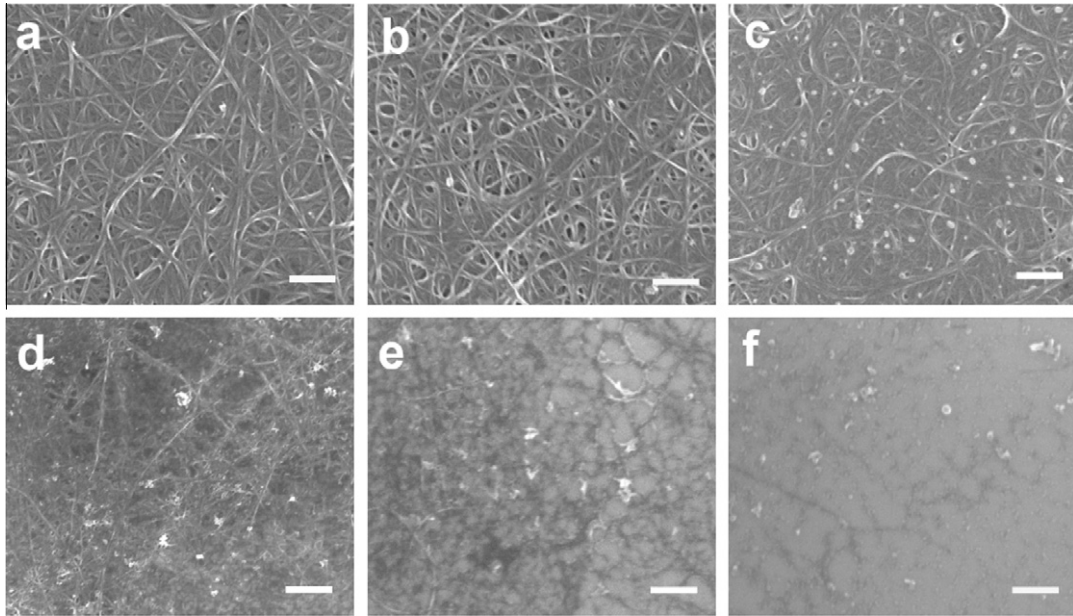


Fig. 3 – Morphology change of a SWCNT TF as a function of ozone treatment time of (a) 0 s, (b) 0.5 min, (c) 1 min, (d) 3 min, (e) 5 min, and (f) 10 min. The scale bar represents 200 nm.

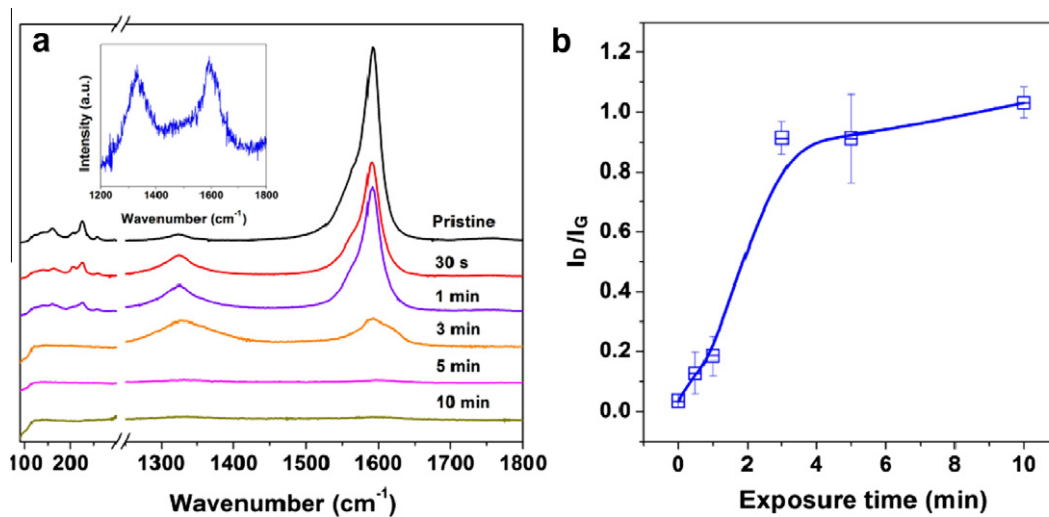


Fig. 4 – (a) Raman spectra and (b) I_D/I_G ratio of the SWCNT TFs exposed to ozone for different times; Inset in (a) is the magnified D and G bands of the sample exposed to ozone for 10 min.

particles and debris can be observed (Fig. 3c). This phenomenon was also found in previously reported plasma etching process [13], and was attributed to etching damage by the oxygen plasma. When the exposure time was increased to 3 min, the amount of amorphous carbon particles and debris increases (Fig. 3d), and the typical morphology of SWCNTs, as seen in Fig. 3a, can be barely distinguished, indicating that strong etching has occurred and the SWCNT network has collapsed. It is worth noting that although some carbon debris is observed, functionalization and etching cause the SWCNT network to lose its electrical conductivity. Therefore, the real-time electrical resistance measurement shows an insulating state of the SWCNT film. When the exposure time

increases to 5 and 10 min, most of the carbon debris is etched away (Fig. 3e and f).

Fig. 4 shows the Raman spectra and I_D/I_G ratio (the intensity ratio of D peak to G peak) change of the SWCNT TF exposed to ozone for different times. Based on the radial breathing mode (RBM) analysis, the diameters of the pristine SWCNTs are in the range 0.9–1.5 nm, and metallic and semi-conducting nanotubes co-exist in the sample [23]. The pristine SWCNTs show a I_D/I_G ratio of 0.035, suggesting the low defects of the SWCNTs. When the SWCNTs are exposed to ozone for 0.5 and 1 min, the I_D/I_G ratios increase to 0.12 and 0.18 despite an undetectable change in the RBM, indicating that defects increase due to the etching and functionalization

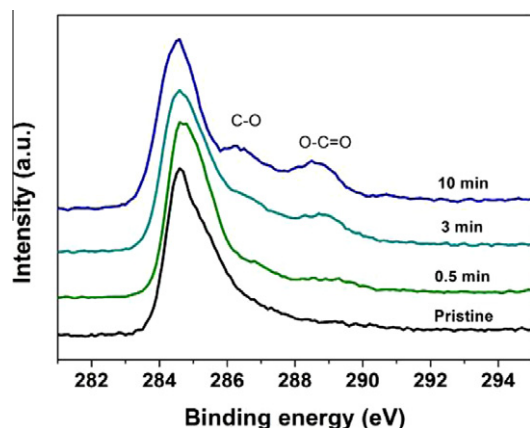


Fig. 5 – XPS spectra of the SWCNT TFs exposed to ozone for 0, 0.5, 3 and 10 min.

of ozone. When the exposure time is increased to 3, 5 and 10 min, the RBM peaks disappear, implying that the SWCNTs lose their tubular structure due to the strong oxidation ability of ozone. It is worth noting that the physisorption of a trace amount of ozone (ppm level) on SWCNTs was reported to result in a decrease of electrical resistance due to chemical doping [24,25], but we did not observe such a phenomenon in our experiments (Fig. 2a). We believe that, when exposed to a high concentration of ozone (~70%), chemisorption dominates, and this damages the π -conjugated structure and increases the resistance of the SWCNTs. The I_D/I_G ratio of the SWCNTs after a 3 min exposure is sharply increased and is saturated at ~0.9, which suggests that highly disordered carbon (amorphous carbon and carbon debris from the SEM observation) is formed by long ozone exposure time.

Fig. 5 shows the XPS spectra of the SWCNT TFs treated using ozone with different times. Prior to ozone exposure, the C1s spectrum is dominated by a single peak at 284.6 eV, showing a characteristic of graphitic carbon; while after ozone treatment, even for the SWCNT TFs exposed to ozone for only 30 s, the XPS spectrum show significant peaks at 286.5 and 289.0 eV, corresponding to the epoxides or hydroxyl bonds and carboxyl bonds, respectively [26], indicating that chemical bonds have formed between carbon and oxygen for a very short exposure time. Since we do not observe a pronounced change in SEM observations and only a slight increase in the I_D/I_G ratio of the SWCNT TF treated for 30 s, we conclude that chemisorption dominates the initial stage. Rapid chemisorption offers more reaction sites for further functionalization and etching. As a consequence, longer exposure times (3 and 10 min) produce stronger peaks at 286.5 and 289.0 eV. These bonds are the results of a transformation from unstable intermediate ozonides which are formed by a cycloaddition reaction between ozone and hexagon carbon rings. During the reaction, CO and CO₂ were liberated as byproducts, causing the etching of SWCNTs [18,21].

Based on the above results, we can explain below why ozone quickly causes the exposed SWCNTs to become insulating and efficiently achieves a SWCNT TCF pattern.

- (i) In the first few seconds, a high concentration of ozone molecules quickly chemisorbs on a SWCNT TF and becomes dominant. Although the network of the SWCNT TF is barely affected (Fig. 3b and Fig. 6a1), its electrical resistance shows a rapid increase (Fig. 2a), and the SWCNT TF shows a slight increase of the I_D/I_G ratio and the presence of C-O bonds. Subsequent chemisorption (Fig. 6a2) damages the π -conjugated

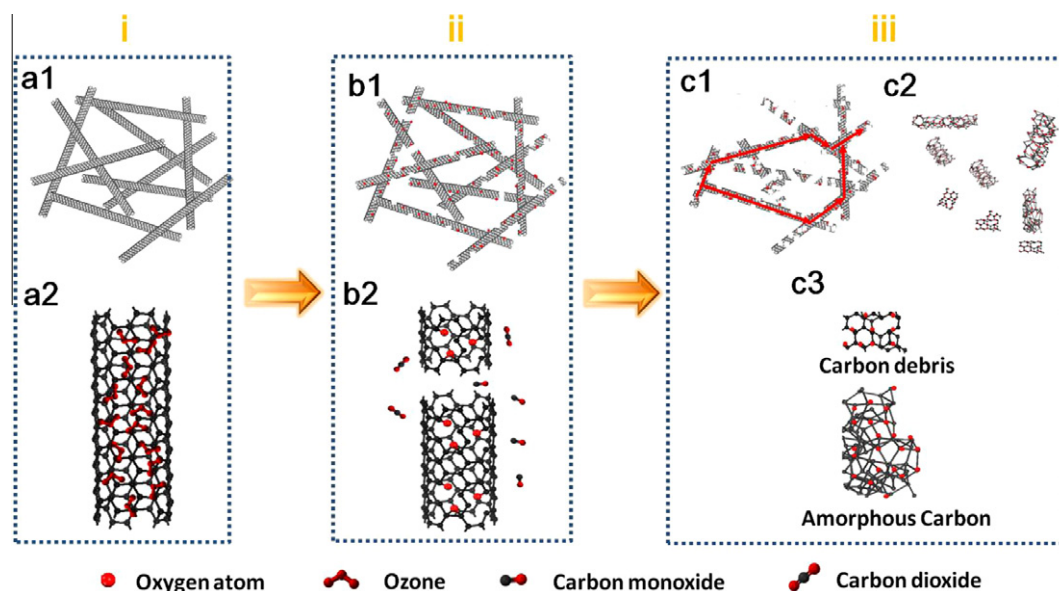


Fig. 6 – Schematic of the evolution of SWCNTs and a SWCNT network upon ozone exposure. In the initial few seconds, (a1) the SWCNT network shows little change, but (a2) ozone starts to chemisorb on SWCNTs. With the exposure prolonging, (b1) the electrical pathways of the network are gradually broken, and (b2) the SWCNTs are heavily functionalized and destroyed. Finally, (c1) the conductive pathways are decreased below the percolation threshold, and (c2) the SWCNT network is destroyed, and (c3) the SWCNTs are etched to carbon debris and amorphous carbon.

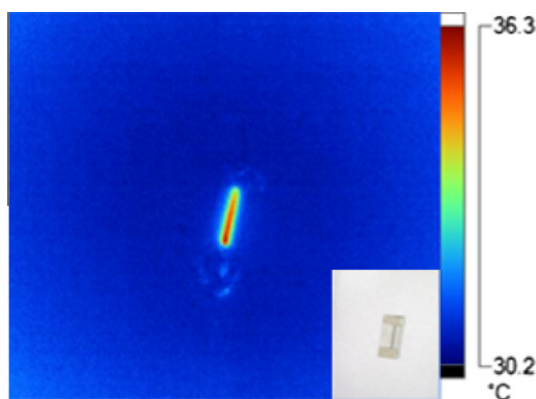


Fig. 7 – The IR image of a line pattern with a 300 μm width after applying a 5 V DC. Inset is the picture of the line pattern.

structure and rapidly increases the electrical resistance of SWCNTs, and offers more reaction sites for functionalization and etching

- (ii) As the exposure increases to 2 min, the SWCNT TF is strongly functionalized and etched (Fig. 6b2). This is supported by the fact that some amorphous carbon exists on the network (Fig. 3c) and the SWCNTs show a higher I_D/I_G ratio and more C–O bonds. However, the resistance shows a slower increase compared to that in the first few seconds. This is because the SWCNT TF contains many electrical pathways formed by entangled SWCNTs and its electrical transport follows the percolation theory. The etching of SWCNTs would lead to a breakdown of the conductive pathways (Fig. 6b1). When the number of such pathways is above the percolation threshold, the electrical resistance will only gradually increase.
- (iii) With the exposure continuing, the electrical transport of a SWCNT network is destroyed below the percolation threshold. SEM observations show that only carbon debris and amorphous carbon are left on the substrate (Fig. 3d–f), and SWCNTs lose their tubular structure based on the Raman characterization. Moreover, the resistance shows a further sharp increase until saturation at around 10 G Ω after exposure to ozone for 3 min. According to the percolation theory, when electrical pathways are damaged to a critical point, where few SWCNTs survive and every pathway is vital for electrical conductivity (Fig. 6c1). In this manner, further etching causes a rapid increase of electrical resistance. Finally, when the remaining conducting pathways are etched away (Fig. 6c2 and c3), the part of the film exposed to ozone becomes insulating. Due to the rapid chemisorption and strong functionalization and etching effect of ozone on the SWCNT network, SWCNT TFs can be quickly and efficiently patterned by photolithography and subsequent OGEE.

For a patterning process, residue in undesired areas is a common problem in scalable production due to insufficient etching [27]. However, using the OGEE method, although some residues exist in undesired areas (Fig. 3e), it is not a

problem for further use because the residues are highly insulating as proved by real-time electrical resistance measurements, Raman and XPS characterization. To further verify the feasibility of the patterning for SWCNT TFs by the proposed method, a 300 μm -wide line pattern was obtained by photolithography and 3 min OGEE, and then connected to a 5 V DC power supply. IR images were then taken by an IR camera. When voltage is applied, the pattern area forms a thermal source due to the Joule heating effect, while the rest area shows no thermal response because of its insulating state. This can be easily distinguished from temperature differences measured by the IR camera. Fig. 7 is the IR image when the voltage was applied for 3 s, and an obvious temperature increase was observed in the patterned area, suggesting an effective conductivity of the pattern. The temperature of the rest area remains unchanged, proving that undesired SWCNT TFs are efficiently etched by ozone and made insulating. Meanwhile, we assembled an EL device by using a “lantern” patterned SWCNT TF as one electrode and applied an AC voltage as high as 500 V. As shown in Fig. S2, no electrical shorts occurred, and the lantern shape could be easily identified without any luminescence in the ozone-treated area, which also strongly demonstrates the effectiveness of this patterning method.

4. Conclusions

We report a simple oxidative gas exposure patterning method combining photolithography and subsequent OGEE to pattern SWCNT TFs on polymeric substrates without using a vacuum and high temperature. After photolithography, clear and uniform SWCNT TF patterns can be obtained by simple ozone gas exposure treatment for several minutes at ambient pressure. SEM, Raman, and XPS characterizations show that ozone can chemisorb on, functionalize and etch the SWCNTs, and then destroy the conductive network of SWCNTs following the percolation theory. This causes a nonlinear resistance increase and a fast breakdown of electrical transport in SWCNT TFs. IR images and an EL device based on the SWCNT TF pattern prove the effectiveness of this patterning approach. This simple and efficient patterning method may have potential for assembling SWCNT film-based electronics, especially for those requiring low processing cost, low temperature, high reliability, and efficiency.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.carbon.2012.08.045>.

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