µ-Patterning of Carbon Nanotube (CNT) forest for MEMS applications

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Abstract. This paper proposes three new approaches for micro patterning of CNT forest in order to make it useful for MEMS based applications. The first two techniques are based on micro electro discharge machining (µ-EDM). However, the biggest problem associated with µ-EDM is the spark gap which limits the structural resolution of the fabricated pattern. In order to overcome this challenge the first technique proposed in this paper is reverse µ-EDMing of CNT forest where the CNTs are used as cathode instead of tungsten tool. This dramatically reduces discharge voltage hence the spark gap. In the second method Sulphur Hexafluoride (SF$_6$) was used as dielectric instead of air which has three time higher dielectric strength than air. This helps to reduce spark gap further. This research work also discusses the experimental results when SF$_6$ was used as dielectric medium for reverse EDMing CNT forest. It was observed that at too low voltage (~10V) air gives lower spark gap than SF$_6$, however at moderately high voltage (~25V) SF$_6$ performs better. Finally, the third approach for patterning CNT forest described in this paper is mechanical bending of CNTs. In this method patterning of CNT forest is carried out by moving a rotating cylindrical µ-tool (3000RPM) in X,Y and Z direction. The Z movement of the tool is controlled in step mode to provide the overall depth of the µ-structures with 1µm/step. In XY plane the tool moves continuously at 1mm/min speed. The movement of the tool on the CNT forest causes the CNTs to be bent and flattened in the direction of the tool motion hence the patterns are formed on bare CNT forest. The most significant observation made from the processed CNT forest is the visible optical reflection from bent and flattened area. Typically, CNT forest is known to be the darkest material on earth. However, this new processing technique causes the CNT surface to reflect light like mirror. A detail comparison between all proposed techniques (mechanical and reverse µ-EDM) for patterning CNT forest is also included in this paper.

1. Introduction

Vertically aligned Carbon Nano Tubes (CNTs) which are commonly referred to as CNT forests is drawing attention by the researchers in the field of micro-electro-mechanical systems (MEMS) because of its very attractive mechanical, electrical, optical, and thermal properties [1-5]. Patterning of CNT forest is very important for MEMS based application and this is currently carried out through selective growth of the forests by chemical vapor deposition (CVD) on pre-patterned catalyst on the
substrate. This method has limitation in producing true 3-D structure. Free-form and three dimensional micro-patterning of CNT forest by micro-electro-discharge machining (µEDM) was first proposed by Takahata group from UBC, Canada \[6, 7\]. Dry air (mixture of \(N_2\) and \(O_2\)) was used as the dielectric medium in the process as liquid dielectric causes damage to the forest because of capillary action. The optimal machining condition was observed at the discharge voltage of 30 V. This technique was further investigated to understand possible removal mechanism of CNTs by µEDM \[7, 8\]. These studies suggest the removal of CNTs during µEDM is carried out by oxygen plasma etching rather by direct thermal removal (evaporation and melting) process. The machining tolerance which is mostly governed by the spark gap was observed to be in a range of 10 \(\mu m\); significantly larger than typical values (of one to a few \(\mu m\)) involved in standard µEDM for metal erosion. In order to achieve high tolerance on a patterned CNT forest by µ–EDM spark gap is a big challenge that needs to be addressed. In this paper two approaches shall be discussed in order to achieve higher tolerance on patterned CNT forest by µ–EDM.

In typical EDM (including µEDM), the workpiece and the electrode are generally arranged to be the positive and the negative, respectively, as this polarity is helpful for efficient EDM operation. CNTs are known to significantly enhance an applied electric field and thus have excellent electron emission properties because of their extremely small tips with nanometer radii and high aspect ratios. Previous report suggests that CNT cathodes can reduce gas breakdown voltage while enhancing discharge current compared to tungsten cathodes \[9\]. This suggests that the use of reverse polarity in µEDM of CNT forests could be effective in lowering the discharge voltage which will be helpful to pattern CNT forest at lower energy thus to reduce the spark gap. This hypothesis is explored experimentally in this present study by carrying out reverse-polarity µEDM of pure CNT forests in dry air.

Dielectric strength plays an important role in µEDM. Sulphur hexafluoride (SF\(_6\)) has a dielectric strength much higher than that of \(N_2\) (by a factor of ~3). This suggests that in SF\(_6\) ambient the gap between the machining electrode and workpiece needs to be much smaller to initiate breakdown for a given electric field strength. This hypothesis suggests that use of SF\(_6\) as the dielectric medium may further reduce the spark gap which will eventually increase the resolution of the patterning of CNT forest by µEDM. This was verified experimentally in this study and discussed in the second part of the paper.

Finally, another approach for patterning CNT forest described in this paper is mechanical bending of CNTs. Patterning of CNT forest is carried out by moving a rotating cylindrical µ–tool (3000RPM) in X,Y and Z direction. The movement of the tool on the CNT forest causes the CNTs to be bent and flattened in the direction of the tool motion hence the patterns are formed on bare CNT forest without any spark gap which is normal µEDM based patterning method.

2. Experimental Setup

CNT forest samples are first grown on highly doped silicon (Si) substrate (<100> n-type) by a method called chemical vapour deposition (CVD). All the experiments related to patterning of CNT forest samples using various methods were carried out using a servo-controlled 3-axis µEDM system with a 0.1-µm positioning resolution. The discharge pulses were generated with a relaxation-type resistor-capacitor (\(R-C\)) circuit \[10\] (for µ-EDM based experiments).

The experimental set-up for reverse µ-EDM in air is illustrated in Fig. 1. As shown, a current probe (CT-1, Tektronix, USA) was used to monitor pulses of the discharge current in real time. The discharge current data were captured from the oscilloscope using a GPIB interface and stored in a computer for subsequent analysis. A series of µEDM experiments at both normal and reverse polarities were performed for various energy levels that were controlled by varying the discharge
voltage in a range of 10-60 V with a fixed capacitance of 10 pF in the \( R-C \) circuit. The electrode (tungsten, diameter of 40-93 \( \mu \)m) was rotated at 3000 rpm during all the machining experiments. The X-Y scanning rate and the electrode feed rate in the Z direction were set to 1 mm/min and 10 \( \mu \)m/min, respectively.

![Figure 1](image1.png)

**Figure1**: Set-up used for characterization of reverse-polarity \( \mu \)EDM of pure CNT forests in air and \( SF_6 \) environment.

Same setup was used (Fig. 1) for \( SF_6 \) based \( \mu \)EDMing of CNT forest. According to the illustration first O\(_2\) was mixed with either N\(_2\)/SF\(_6\) inside a buffer chamber, and the mixed gas was introduced to the machining chamber, where the O\(_2\) concentration was measured using an oxygen sensor (VN202, Vandagraph Co., UK). The flow rates of O\(_2\) and N\(_2\)/SF\(_6\) was adjusted so that the O\(_2\) concentration reached the target value and was stabilized in the machining chamber for at least 5 minutes prior to machining. A series of \( \mu \)EDM experiments (with \( SF_6 \)) were performed using cylindrical tungsten electrodes rotating at 3000 rpm. The \( \mu \)EDM conditions are summarized in Table 1. A 10-pF capacitor was used in the discharge circuit for all the experiments in this study.

| Parameters                             | Values used                              |
|----------------------------------------|------------------------------------------|
| Machining voltage (V)                  | 25 or 10                                  |
| Capacitance (pF)                       | 10                                       |
| Electrode feed rate during EDM (mm/min)| Z: 0.03, X-Y: 1                            |
| Ambient O\(_2\) % in \( SF_6 \) (for the \( SF_6\)-O\(_2\) system) | 50, 20, 10, 0, or 0                        |
| Ambient O\(_2\) % in N\(_2\) (for the N\(_2\)-O\(_2\) system) | 20 or 0                                   |

Finally Fig.2 illustrates the concept of mechanical processing of the CNT forest that is locally bent by scanning a microscopic metallic tool; a cylindrical piece of tungsten (diameter \( \leq 300 \) \( \mu \)m) rotating at a speed of 3,000 rpm is moved along the X, Y, and Z directions to carry out the process. This experiment was also performed on the same machine as mentioned earlier. However, in this case the EDM power was turned off during patterning. The movement in the Z direction was performed in the step mode with a step size of 1 \( \mu \)m, and the back-and-forth scanning speed in X and Y directions was 1 mm/min.

![Figure 2](image2.png)

**Figure 2**: Concept of patterning CNT forest by mechanical bending of CNTs.
3. Results and Discussions:

3.1 Reverse polarity μEDM in air:

In this section results related to reverse polarity μEDMing of CNT forest (in air medium) have been discussed. At first discharge pulses generated with both reverse and normal polarities were characterized to observe the differences between the two conditions. Fig.3 shows the comparison of the average peak current of the pulses (n = 400) measured at different voltage levels. It can be understood from the comparison that the peak currents with the reverse polarity are higher than those with the normal polarity, and that the difference in the peak current at lower voltages is significant.

Figure 3: Average peak current of discharge pulses measured at different voltages (with 10-pF capacitance).

A possible reason behind the higher discharge current in the reverse-polarity case that uses the forest as the cathode could be enhanced field-emission (FE) from CNTs [11]; the forest cathode can more easily emit electrons from the nano-scale tips of the CNTs compared to a conventional metallic cathode (such as the tungsten tip) at a given voltage.

The previous studies reported that the lowest value of the optimal voltage with the normal polarity was around 30V, and that further lowering of the voltage led to mechanical grinding of the CNTs [6]. To evaluate the effect of the reverse polarity at low voltage, square patterning with both polarities were carried out at 10 V and 10 pF. The results in Figs. 4(a) and 4(b) indicate that the reverse-polarity process produced sharper, smoother, and cleaner microstructures compared to the normal-polarity case. Moreover, the patterns created with the reverse polarity exhibited a narrower width in the machined grooves compared to those with the normal polarity even though identical electrode and machining conditions were used. From the dimensions shown in Fig. 4, as well as the diameter (93 μm) of the electrode used, the discharge gap clearance is calculated to be 7.5 μm for the normal polarity, whereas for the reverse polarity it is 2.5 μm, which is 3× smaller (and shows a ~4× improvement over the previous result reported in [6]). This means that reverse μEDM enables much tighter tolerances and higher precision in CNT forest patterning.
Figure 4: SEM images show micropatterns machined in a CNT forest using 10 V for a depth of 40 μm with (a) normal polarity and (b) reverse polarity.

Machining stability is another important aspect of μEDM processing of CNT forests. In the process, electrode feeding is feedback controlled so that when a short circuit is detected, the Z stage retracts the electrode upward until the circuit is opened and then moves the electrode downward to resume its feeding and the machining process. The process becomes unstable and slow if many short circuits occur during the process because of frequent up/down motion of the Z axis. It was observed that reverse-polarity machining at low voltages was consistently more stable than normal-polarity machining for CNT forests. This tendency can be seen in Fig. 5 that plots the electrode position on the Z axis during each of the machining processes conducted under the same conditions except for the voltage polarity. It is clear from the graph that the normal-polarity case produced frequent short circuits that led to ripples in the electrode motion, whereas the reverse-polarity case resulted in much more stable and faster electrode feeding or removal of the CNTs. For this particular machining condition, the total machining time with the reverse polarity was approximately 60 % shorter than the time with the normal polarity.

Figure 5: Electrode positions on the Z axis tracked in real time during machining with normal and reverse polarities, both using the same machining condition.
The effectiveness of low-energy reverse $\mu$EDM in high-aspect-ratio micromachining of CNT forests was evaluated by patterning conical and pyramid like microstructures at the same EDM condition (10V and 10 pF) using a tapered cylindrical electrode as shown in Fig. 6.

**Figure 6:** SEM images of high-aspect-ratio microstructures patterned using reverse $\mu$EDM at 10V by scanning a cylindrical electrodes along a circular or square orbit: (a) A needle-like microstructure with an aspect ratio of ~25; (b) a deep pyramid structure.

### 3.2 Reverse polarity $\mu$EDM of CNT forest in SF$_6$ medium:

In order to further enhance the resolution of the micro structures patterned by EDM on CNT forest gaseous medium with high dielectric strength (SF$_6$) was used. In this section experimental result using SF$_6$ ambient shall be discussed. To study the role of O$_2$ in the SF$_6$ case, the $\mu$EDM process was characterized with O$_2$ concentrations of 10%, 20%, and 50%. The results machined at 25 V shown in Fig. 7 suggest that the structural and surface quality improved with increasing O$_2$ concentration up to 20% (Fig. 7(a) and (b)), and that the structures became distorted (e.g., the top surface of the centre post as seen in Fig. 7(c), possibly due to sparks propagating and etching portions of it) again when the concentration was further increased to 50%. The structure machined at 10 V and 20% O$_2$ in SF$_6$ shown in Fig. 7(d) indicates deteriorated structural quality compared to Fig. 7(b), the 25-V case under the same ambient. The results obtained at the same voltage levels, 25 V and 10 V, with 20% O$_2$ in N$_2$ ambient are shown in Fig. 7(e) and (f), respectively. These suggest that, in contrast to the SF$_6$-O$_2$ ambient cases, the 10-V condition led to higher machining quality than the 25-V condition in the N$_2$-O$_2$ ambient; this result is consistent with the previous findings reported in [6]. However, a comparison between Fig. 7(b) and (f), representing the conditions that provided the highest machining quality for the SF$_6$ and N$_2$ environments, respectively, suggests that SF$_6$ results in sharper corners (without extended portions at the corner of the centre post) than N$_2$, and the sidewall of the resultant structure is smoother (free from extended layers) for SF$_6$ ambient. Possible sources of the different optimal voltage levels for the SF$_6$ and N$_2$ environments (25 V and 10 V, respectively) found above will be discussed later.
Figure 7: SEM images of the microstructures machined in a CNT forest: (a) 10% O$_2$ in SF$_6$ at 25 V; (b) 20% O$_2$ in SF$_6$ at 25 V; (c) 50% O$_2$ in SF$_6$ at 25 V; (d) 20% O$_2$ in SF$_6$ at 10 V; (e) 20% O$_2$ in N$_2$ at 25 V; (f) 20% O$_2$ in N$_2$ at 10 V.

Fig. 8 shows, in SF$_6$ (at 20% O$_2$), processing at 25 V resulted in the minimum discharge gap and the highest machining quality; however, this is not the case for N$_2$ (at the same O$_2$ concentration), in which processing at 10 V led to the minimum gap and the highest machining quality. In the SF$_6$ environment, 25 V was a suitable voltage level to produce spark discharge pulses and perform smooth machining (Fig. 7(b)); however, 10 V may have made the discharge gap too small because of the high-dielectric ambient and thus caused physical touching and mechanical rubbing between the rotating electrode and the forest surface (which may have caused the circular marks on the bottom of the structure shown in Fig. 7(d) due to non-ideal mechanical/positioning instability in the µEDM system used, deteriorating the processed structure/surfaces. This undesired mechanical contact may have also occurred on the sidewalls of the patterned structures and caused slight bending or displacement of the CNTs on the walls, which may be the probable cause of the larger gap compared with the N$_2$ environment case at 10 V (Fig. 7(d)).

Figure 8: Measured discharge gaps resulted from the SF$_6$ and N$_2$ environments (with 20% O$_2$) and two different discharge voltages.
With a discharge voltage of 25 V and an O\textsubscript{2} concentration of 20\%, the use of SF\textsubscript{6} was revealed to give better results compared to N\textsubscript{2}, the conventional ambient medium; the discharge gap could be reduced to 4.2 \(\mu\)m. At a lower voltage level (10 V), an N\textsubscript{2} ambient with 20\% O\textsubscript{2} produced an even smaller discharge gap, although the occurrence of short circuits slowed the removal process somewhat.

### 3.2 Patterning of CNT forest by mechanical bending:

Finally to eliminate completely the spark gap problem associated with EDM based patterning method efforts were made to pattern bare CNT forest by mechanical bending of CNTs. The process is described in the section 2 earlier. In this method the spark gap was zero as no spark erosion was taken place during the process. However another significant observation made from the patterned CNT forest is the reflectivity from bent and flattened CNT forest. Typically, CNT forest is known to be the darkest material on earth. [12]. However, when mechanical processing technique is applied on the CNT forest it starts to reflect light like mirror as shown in Fig. 9(a). The reflectivity of the surface was measured and quantified and the result is shown in Fig. 9(b). The result shows the bent region of the CNT forest has optical reflectivity in a range of 10\% to 15\% from visible to infrared spectrum of light, which is two orders of magnitude higher than bare CNT forest.

![Figure 9](image)

**Figure 9:** (a) Optical image showing the reflected image of the tool on the bent-CNT surface. (b) Measured normal-incidence spectral reflectance of the surface (averaged) for visible-near infra-red light accompanied by images of red, green and blue light reflection from the processed surface.

The possible reason behind the observed reflectivity from the bent CNT surface is stated as follows. The CNTs of the grown forest are essentially Multi-walled CNTs (MWCNT), hence metallic. When they are bent and flattened by the moving tool a nice smooth surface texture is created with surface roughness S\textsubscript{a} as low as 5nm (shown in Fig. 10). This surface roughness is of optical quality. Therefore, the processed metallic CNT surface starts to reflect light.

![Figure 10](image)

**Figure 10:** AFM result of the surface shows high quality surface finish with S\textsubscript{a} 5nm and S\textsubscript{y} 0.1 mm.
4. Conclusion:
Post patterning of CNT forest is necessary in order to use it for MEMS based applications. In this paper three methods for micro patterning of CNT forest have been discussed. First two methods are μEDM based technology. It was shown for μEDM based patterning method, reverse EDM with high dielectric environment (SF₆) can reduce spark gap at a voltage level of 25V however if the voltage is reduced further down (~10V) then reverse EDM in air proved to produce low spark gap with significantly long machining time. Mechanical patterning method can eliminate spark gap problem completely with high quality surface roughness (Sa = 5nm). Though, this method flattens the protruded CNTs on the patterned path. Therefore, it may not be suitable where protrusion of CNT in patterned zone is necessary.

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