

Wire Electrical Discharge Machining of Carbon Nanofiber Mats for Field Emission

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This study describes wire electrical discharge machining (WEDM) of carbon nanofibers (CNFs) in air. Since EDM is able to machine any conductive material, it can be used to machine CNFs without causing physical damage. WEDM was applied for leveling and patterning of CNF mats, which improves the performance of field emission of CNFs. For WEDM, a wire jig system as well as debris-removing system was developed. The machining characteristics such as the effect of voltage and capacitance were investigated. WEDM in air was used for the post processing of CNF mats with high efficiency and productivity. Compared to EDM using a single tool electrode, WEDM reduced machining time to 1/10th of the previously required time.

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1. Introduction

Carbon nanofibers (CNFs) consist of graphite layers having a cylindrical or conical stack structure. Their diameters vary from a few to hundreds of nanometers and their lengths range from less than a micron to several millimeters.¹ CNFs act as field emitters because their aspect ratios are very high and they require only low threshold voltages in order to emit electrons. In addition, CNFs have good mechanical and chemical properties. As shown in Fig. 1, CNF films can be used in a field emission display in which electrons are emitted as a result of the tunneling effect when high voltage is applied to the material.² CNFs are preferred for field emission since they require a lower threshold voltage, and are more uniformly aligned with respect to other emitting surface materials. For the purpose of obtaining a more uniform flat surface, post-processing methods such as laser irradiation, plasma treatment, chemical treatment, and mechanical processing were investigated.³⁻⁶

Recently, micro electrical discharge machining (micro EDM) of CNFs was also introduced.⁷⁻¹² CNFs can be machined by EDM regardless of their mechanical and chemical properties because the method is a thermal process by discharging.¹³ EDM involves non-contact machining, and as a result the CNF film is free of flaws

which could otherwise occur from damage caused by physical contact. The process involved is relatively simple. Ok et al. reported that Micro EDM can be used to machine CNFs to uniform height which will result in overall enhancement of CNF field emissions.⁷ The leveling of CNFs was conducted under the condition of 100 V and stray capacitance using a \varnothing 1 mm cylindrical electrode. On the other hand, it was reported that specific patterning of CNF films can also improve their field emission.⁹ The patterns on the CNF film were machined by EDM in order to achieve higher field emission intensity. A \varnothing 100 μ m electrode tool was fed in the X-Y directions with a pitch of 350 μ m to form square-shaped patterns. Takahata et al. also used the EDM process to machine high-aspect ratio patterns on carbon nanotube forests.^{11,12}

In previous studies, a single cylindrical tool electrode was used. However, using this method involves excessive machining time since the tool paths involve very complex micro patterning. Also debris resulting from the CNFs becomes attached to the tool electrode or the CNF mats during the machining which prevents uniform machining of the surface. To solve these problems, wire electrical discharge machining (WEDM) was applied to the CNF film and a debris-removing system was attached. The effects of voltage and capacitance were also studied in order to enhance the performance of field emission by CNF machining using WEDM.

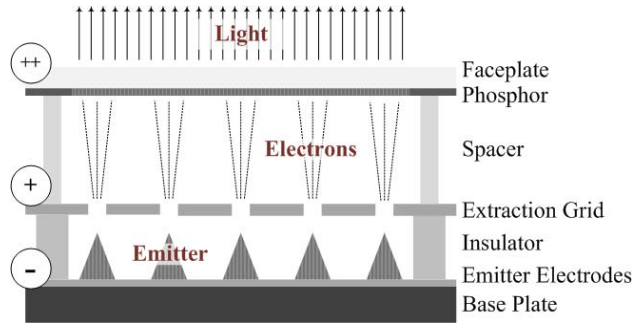


Fig. 1 Schematic of field emission display

2. Experimental System

Fig. 2 shows the schematic diagram of micro WEDM. A tilting stage is attached above the X-Y-Z stage and a wafer, on which the CNF film is grown, is installed on the stage. The voltage is applied between a wire and the CNF film, and then the wire is adjusted along Z until it is optimized with respect to the CNF film. When the gap between the wire and CNF film is sufficiently small, discharge occurs and the CNFs are then machined.

To machine the CNF film uniformly, it is very important that the wire be placed parallel with X-Y plane of the stage. If this is not optimized, the discharge gap required for EDM cannot be maintained continuously along the whole CNF and electric shorts will occur resulting in failure to complete the machining. To align the wire, a tilting stage and a customized wire jig were attached as shown in Fig. 3. The tilting stage was fixed on a surface plate which compensated for the misalignment of the wire to a tolerance of less than $5\ \mu\text{m}$ along a 20 mm length of the X- and Y-axis, respectively. A $\text{Ø} 20\text{-}100\ \mu\text{m}$ tungsten wire was used as the electrode. The distance between the two wire guides was 25 mm and tension was applied to the wire by means of a tension spring in order to prevent vibration of the wire during the machining process.

In a conventional micro EDM, a dielectric fluid such as oil and water is used. However, the fluid can damage or contaminate the CNF film, and it is difficult to remove the dielectric fluid from the CNF after machining is complete. Thus, the micro EDM in this study was performed in air, which is typically referred to as dry EDM. Dry EDM has many advantages; electrode tool wear is very small or negligible relative to the wear encountered in conventional EDM and the machining rate is relatively faster. The machining system is simple because additional equipment such as a water tank is not necessary.¹⁵ In typical dry EDM, pressurized air is used to blow off the molten metal after the spark discharge. However, since CNFs are very thin and flexible, they can be damaged by pressurized air flow. For this reason, pressurized air was not used. Table shows the advantages of dry EDM of CNFs.

CNFs are machined very easily using small discharge energy. Therefore, an RC circuit, which has the advantage of producing small machining energy, was used as the discharge circuit. In EDM of metal, the feed of the tool electrode is adjusted on the basis of the discharge voltage or current. However, it is important to note that CNFs are easily damaged by mechanical contact with the wire.

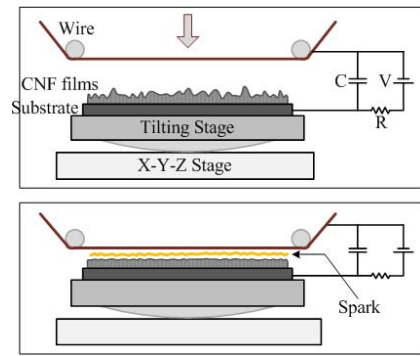


Fig. 2 Schematic diagram of WEDM for CNF film

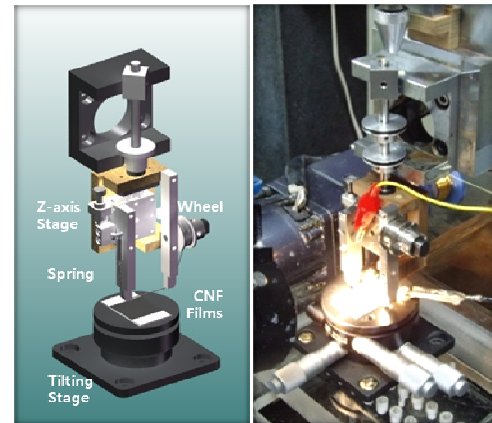


Fig. 3 Wire EDM system

Table 1 Dry EDM of CNF

Features	Advantages
Thermal process	Independent on properties
Non-contact	Free from physical damage
Machining in air	Free from chemical contamination
Simple process	Practicable & flexible
Very small machining force	Precisely controllable
Tool wear	Negligible

Table 2 Machining conditions

Features	
Circuit	RC circuit without feedback
Tool electrode	$\text{Ø} 20\text{-}100\ \mu\text{m}$ tungsten wire
Workpiece	CNF films on wafer
Feed rate	Up to $100\ \mu\text{m/s}$
Voltage	30 V-100 V
Capacitance	From stray capacitance to 10000 pF

Therefore the feed rate of the wire was fixed so that it was low enough to insure that contact did not occur without feedback.

In previous research of EDM using a single cylindrical electrode, the lateral feed rate was on average $200\ \mu\text{m/s}$.⁷ In WEDM of CNF, the feed rate was $100\ \mu\text{m/s}$. The unit machining volume of WEDM was much more than that of EDM which uses a single electrode. In WEDM, a lower voltage of 50 V was used. In EDM process, the shorts were due to debris which had attached to the bottom surface of the tool. Since the diameter of the cylindrical tool is large ($\text{Ø} 1\ \text{mm}$) in the previous research, it is not easy for debris to form outside of the tool. In WEDM, however, the diameter

of the wire is only 50 μm . Therefore, debris can form more easily outside of the machining area. As a result, the material removal rate in WEDM must be higher than that for EDM which uses a cylindrical tool. Table shows the machining conditions in WEDM.

CNFs were synthesized on a 20 mm \times 20 mm wafer by thermal chemical vapor deposition (thermal CVD).¹⁴ A 30 nm thick Cr layer and a 300 nm thick Cu layer were deposited on the silicon substrate via thermal vacuum evaporation. The Cr layer which was located between the Cu layer and the silicon substrate served as an adhesion layer and the Cu layer worked as a seed layer for the subsequent electroplating. The copper micro-tips were then formed through high current pulse electroplating. The solution for the copper electroplating contained copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), sulfuric acid (H_2SO_4), and hydrochloric acid (HCl). Electroplated copper micro-tips showed a vertically aligned sharp geometry and a sparse distribution. Each tip diameter was 30-50 nm and the overall length was about 5-10 μm . A 50 nm thick W layer and a 20 nm thick Ti layer were subsequently deposited upon the copper micro-tip layer via RF/DC sputtering, where the W layer worked as a protection layer against thermal damage on the copper micro-tips while the Ti layer acted as a buffer layer to prevent diffusion of Ni catalysts. Finally, a 10 nm thick Ni layer was formed through thermal vacuum evaporation and served as the topmost layer to furnish catalysts for the synthesis of CNFs. This specimen was placed in a thermal CVD chamber, the temperature was ramped to 600°C. NH_3 and C_2H_2 gas was introduced into the chamber for 5 min and 20 min, respectively. The as-grown CNFs had the appearance of entangled rope, the strands of which had an average height of 50-70 μm .

3. Experiment of CNF Machining

3.1 Basic experiment

Fig. 4 shows the machining of CNF film using a wire electrode. When CNFs were machined in air, sparks were observed and the appearance of the machined CNF was distinct from that of an original CNF in shape. According to the Raman spectral analysis as shown in Fig. 5, CNFs before and after EDM have the same properties.¹³

3.1.1 Characteristics of discharging voltage

Fig. 6(a) shows the typical discharging voltage signal of EDM. When a voltage, V_0 is applied to the wire and CNFs, a discharge takes place under a certain voltage, V_c . After discharge has occurred, the dielectric is restored and the cycle repeats. Fig. 6(b) shows the discharging voltage measured by an oscilloscope in WEDM of CNF film. This figure shows the discharge characteristics of CNF are not different from those which are typical for EDM.

3.1.2 Effect of applied voltage

The effect of applied voltage was investigated. Referring to previous research, voltage from 30 V to 100 V was used. \varnothing 50 μm wire and stray capacitance were used as a tool electrode and a capacitor, respectively.^{8,9} If the applied voltage was less than 40 V,

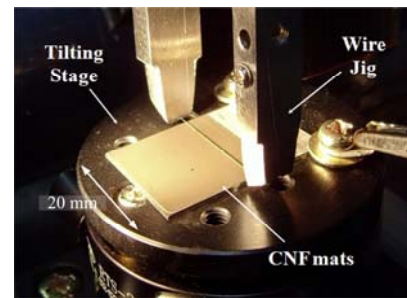


Fig. 4 Wire EDM system for CNF machining

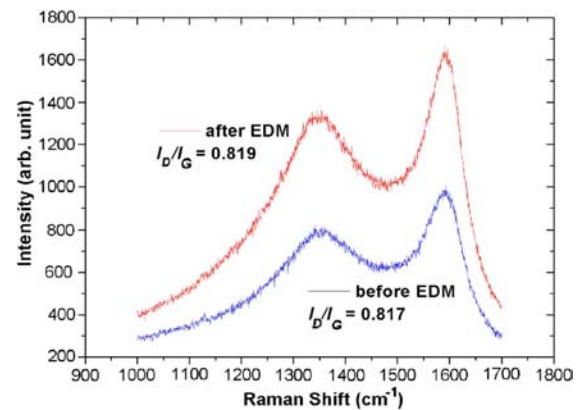
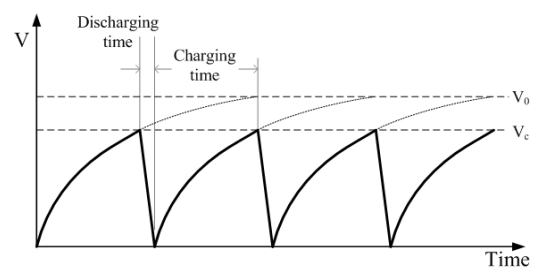
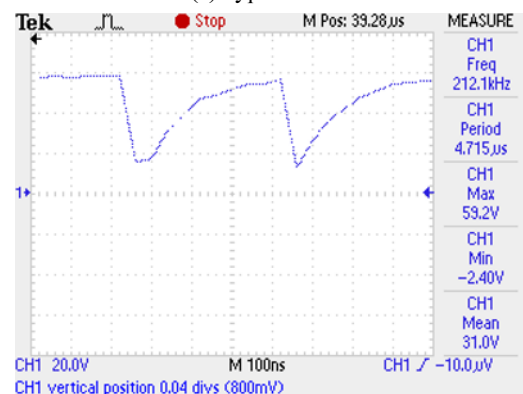


Fig. 5 Raman Spectra of CNF before and after EDM



(a) Typical EDM



(b) Wire EDM of CNF

Fig. 6 Discharging voltage with time by oscilloscope

the discharge energy was too small and it was difficult to machine the CNFs properly and the feed rate was too slow. Fig. 7 shows micro grooves which were machined using different voltages. In the figure, the yellow circles indicate the diameter of the wire. As voltage increased, the machining gap or overcut also increased. At 50 V, a sufficiently small machining gap was obtained and machining was stable.

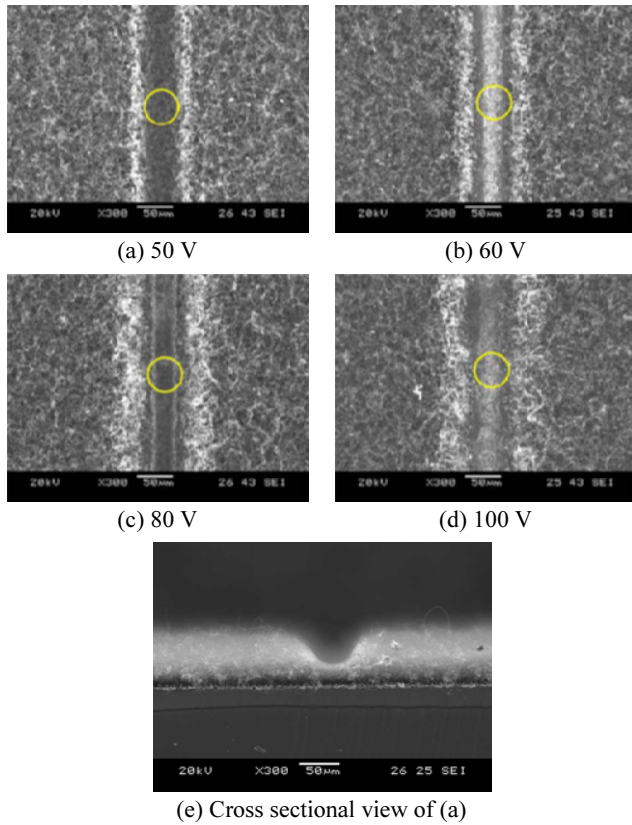


Fig. 7 The machining gap according to the voltage (\varnothing 50 μ m wire, stray capacitance)

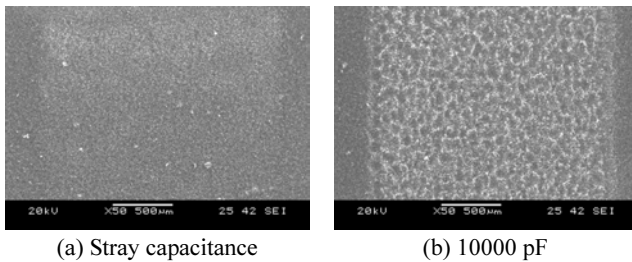


Fig. 8 The machined surfaces according to the capacitance (\varnothing 50 μ m wire, 80 V)

3.1.3 Effect of applied capacitance

The effect of applied capacitance was investigated. Fig. 8 shows the machined surface as it relates to the applied capacitance. The craters became larger and the surface roughness increased as the applied capacitance increased. Since both the voltage and capacitance affect the discharge energy, they need to be minimized in order to achieve better surface uniformity of the CNFs. However, the use of voltages which are too small will not produce the necessary stable discharge. Therefore, it is more advantageous to minimize the capacitance rather than the voltage. The use of stray capacitance was suitable for good uniformity of CNFs.

3.2 Energy dispersive spectroscopy analysis

In conventional EDM, the metal comprising the tool electrode adheres to the machining area of the work piece. Since wear particles from the wire material can deteriorate the CNFs mats, the surface of the CNFs mats were investigated using energy dispersive

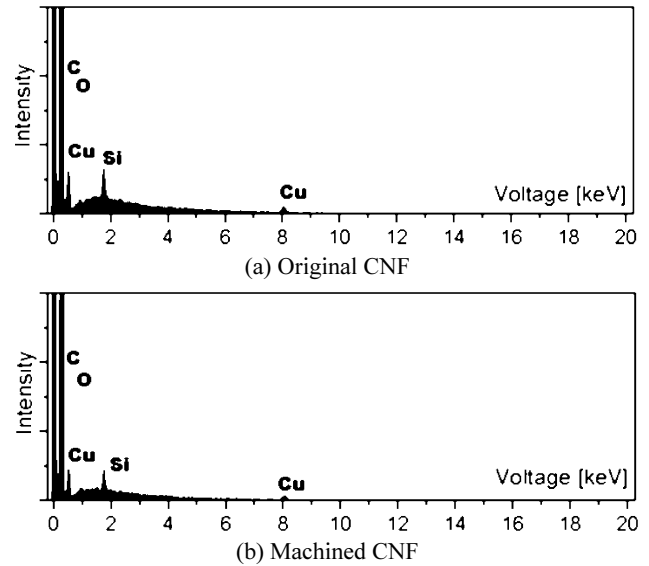


Fig. 9 EDS analysis results of CNFs

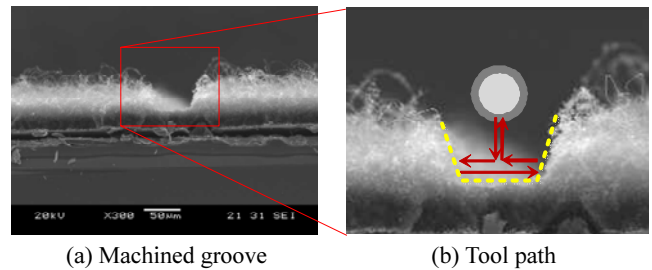


Fig. 10 Sectional image of machined groove (\varnothing 20 μ m, 50 V, stray capacitance)

spectroscopy (EDS) to see if the wire material, tungsten, could be detected on the CNF film. Fig. 9(a) is the analysis resulting from the original CNFs, and Fig. 9(b) is from the machined CNFs. The results from the two parts were the same, which would indicate that the contamination from the wear particles of the wire electrode after EDM is negligible. Since the machining of CNFs does not require high discharge energy compared to the machining of metal, the wear of the wire was insignificant. In conventional EDM, the discharge spark causing high temperature melts the workpiece material and also results in the evaporation of the dielectric fluid at the discharge spot. The evaporation generates high explosive pressure, which helps to remove the molten material. However, since WEDM of CNFs was conducted in air, not dielectric fluid, the molten material from the wire could easily re-solidified on the tool surface. As a result the wear on the wire will be decreased.

3.3 Taper reduction

Since the wire electrode has the round shape, the machined groove become round. In addition, the size of upper section increased further resulting in taper shape because of secondary discharges as shown in Fig. 7(e). The taper shape is not good for field emission performance because the edge of the groove is not sharp. In order to remove taper shape, the small wire electrode (\varnothing 20 μ m) moved horizontally as shown in Fig. 10. Compared to the machined result with the \varnothing 50 μ m wire shown in Fig. 7(e), the taper

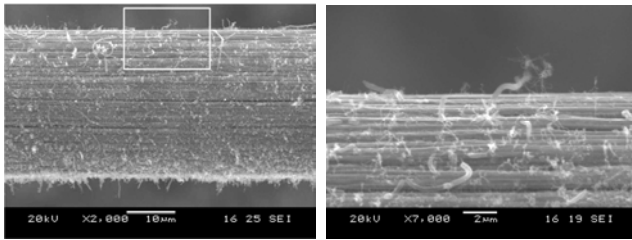


Fig. 11 CNF debris attached on wire after machining

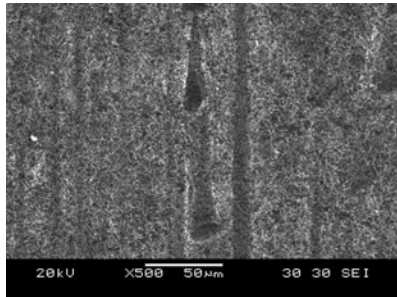


Fig. 12 Scratches on CNF mats caused by the discharge between debris on wire and CNF mats

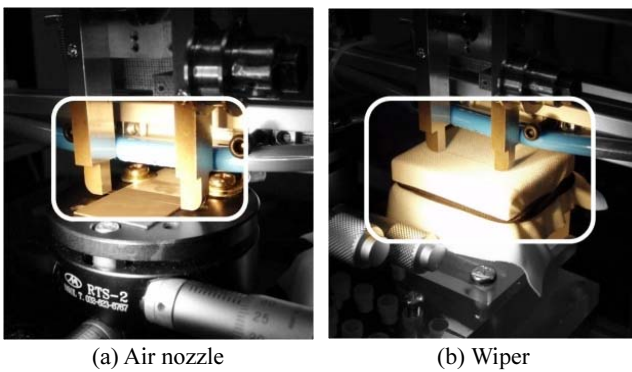


Fig. 13 Debris removing system using air nozzle and wiper

was reduced. However, the small wire requires careful handling because it is very easy to break.

3.4 Debris removing

During WEDM of CNFs, a lot of debris builds up on the wire electrode as shown in Fig. 11. Although the size of the debris particles is very small compared to the wire, the CNF debris can cause some problems; the short circuit occurs and the discharge which occurs between the debris on the wire and the CNF mats degrades the uniformity of the machining surface. If the debris which builds up on the wire is not removed appropriately, scratches on the surface of CNF mats will result as shown in Fig. 12. The scratches are generated by the spark discharge between the debris buildup and CNF mats. Therefore, a debris removing system was attached as shown in Fig. 13. As shown in Fig. 13(a), a nozzle was placed near the wire. Compressed air flowing through the nozzle blows off the debris adhering to the wire during the machining. In addition, the remaining debris was removed by a dustproof wiper as shown in Fig. 13(b). The wiping took only 5-8 seconds. Fig. 14 clearly shows that the debris was effectively removed by this system; Fig. 14(a) shows a wire before the machining, and (b) is the

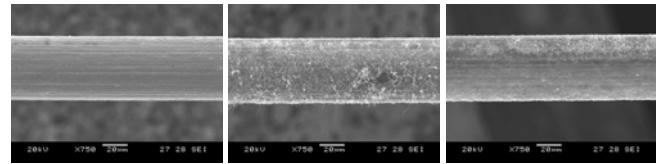


Fig. 14 Tungsten wire before and after debris removing

Table 3 Machining characteristics according to electrode types

	Cylindrical	Wire
Machining area	20 mm × 20 mm	
Machining layer	2 steps by 10	layer
Feed rate	200 μm/s	100 μm/s
Times of travel	80	2
Travel length	1640 mm	40 mm
Times of wiping	80	2
Machining time	About 157 min	About 8 min

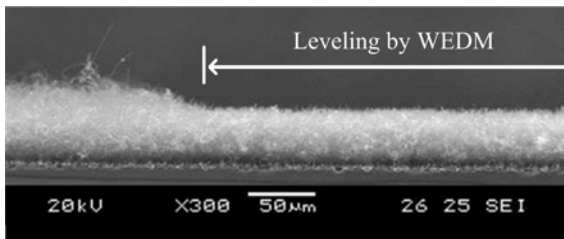
wire after the machining. Fig. 14(c) shows a wire after the debris has been removed. It is clear that this system has successfully removed the debris. In spite of the success of the system for debris removal it must be taken into consideration that some debris will fall down on the CNF mats. However, it is minimal.

3.5 Leveling of CNF film

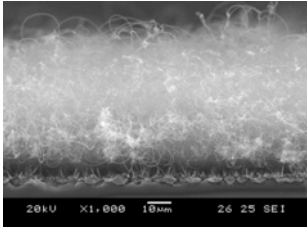
In order to compare the efficiency of WEDM with that of EDM, leveling of CNF films was conducted as shown in Fig. 15. This machining helped to enhance the performance of field emission by making CNFs flat.⁷ In previous research, a single cylindrical tool electrode was moved in a zigzag pattern to machine a CNF film.^{7,8} As a result, it took much time to flatten the CNF film and the tool path used was very complex. By comparison the single tool, the use of a wire electrode can machine CNF mats more effectively. It can flatten the whole CNF film by the use of a uni-directional feed of wire. CNFs were machined layer-by-layer with a 10 μm machining depth considering the diameter of the wire electrode and the removal rate. The lateral feed rate was fixed to 100 μm/s. The tool path was very simple, just coming and going, which prevented cusps which had formed in EDM with the use of a cylindrical tool. Table shows machining characteristics according to electrode types. Consequently, the machining time by wire electrode was reduced by 20 times compared to that by cylindrical electrode. Fig. 15 shows the result of leveling.

3.6 Lattice patterning of CNF film

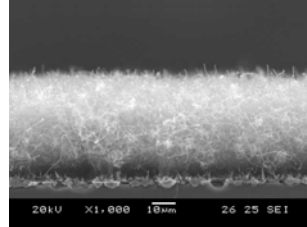
The leveling of CNF films enhances the uniformity of field emissions. However, the leveling makes CNFs shorter. As a result, the intensity of field emission for these shorter CNFs is relatively smaller. On the other hand, the micro lattice-pattern of these CNF films increases the intensity of the field emission.⁹ In this experiment, the patterning of the CNF emitters was performed by WEDM in air. A Ø 50 μm wire electrode was used in patterning by feeding the wire in the Z-direction with 100 μm pitch to form square-shaped patterns. Since the removal rate is larger and it is harder to machine the dense CNFs, the feed rate for the wire was



(a) Leveled CNF film

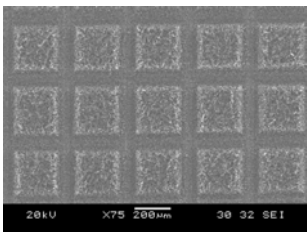


(b) Before the machining

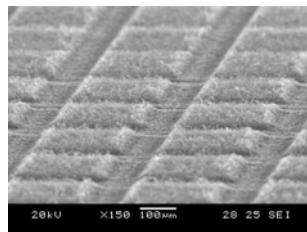


(c) After the machining

Fig. 15 Leveled CNF film



(a) Top view



(b) Tilting view

Fig. 16 Patterned CNF film

decreased to 2-10 $\mu\text{m/s}$. The lattice patterns were machined precisely ($300 \mu\text{m} \times 300 \mu\text{m}$) as shown in Fig. 16. Compared to previous research, the tool travel length was reduced to about 1/1000, while the machining speed was decreased to 1/100 of those of EDM with a single tool electrode. Consequently, the total productivity was increased by a factor of 10.

4. Conclusion

For the purpose of improving the efficiency in micro EDM of CNF film, WEDM of CNF film was investigated. Compared with previous research on CNF machining using a single tool electrode, WEDM reduced the machining time to 1/10th of its previous value, and the overall process was simplified. The best machining quality to date occurred under the conditions of 50 V with stray capacitance where a $\varnothing 50 \mu\text{m}$ wire was used in leveling and a wire less than $50 \mu\text{m}$ in size was used in patterning. WEDM can machine micro features on CNF mats. It can be used as an alternative method to fabricate a customized CNF product. This process is simple and flexible, and can be applied in conjunction with additional treatments of CNF films.

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REFERENCES

1. Melechko, A. V., Merkulov, V. I., McKnight, T. E., Guillorn, M. A., Klein, K. L., Lowndes, D. H. and Simpson, M. L., "Vertically aligned carbon nanofibers and related structures: Controlled synthesis and directed assembly," *J. Appl. Phys.*, Vol. 97, No. 4, Paper No. 041301, 2005.
2. Temple, D., "Recent progress in field emitter array development for high performance applications," *Mater. Sci. and Eng. R: Reports*, Vol. 24, No. 5, pp. 185-239, 1999.
3. Chen, K. F., Chen, K. C., Jiang, Y. C., Jiang, L. Y., Chang, Y. Y., Hsiao, M. C. and Chan, L. H., "Field emission image uniformity improvement by laser treating carbon nanotube powders," *Appl. Phys. Lett.*, Vol. 88, No. 19, Paper No. 193124, 2006.
4. Zhi, C. Y., Bai, X. D. and Wang, E. G., "Enhanced field emission from carbon nanotubes by hydrogen plasma treatment," *Appl. Phys. Lett.*, Vol. 81, No. 9, pp. 1690-1692, 2002.
5. Lim, S. C., Jeong, H. J., Park, Y. S., Bae, D. S., Choi, Y. C., Shin, Y. M., Kim, W. S., An, K. H. and Lee, Y. H., "Field-emission properties of vertically aligned carbon-nanotube array dependent on gas exposures and growth conditions," *J. Vac. Sci. Technol. A*, Vol. 19, No. 4, pp. 1786-1789, 2001.
6. Kim, K. B., Song, Y. H., Hwang, C. S., Chung, C. H. and Lee, J. H., "Efficient electron emissions from printed carbon nanotubes by surface treatments," *J. Vac. Sci. Technol. B*, Vol. 22, No. 3, pp. 1331-1334, 2004.
7. Ok, J. G., Kim, B. H., Sung, W. Y., Chu, C. N. and Kim, Y. H., "Uniformity enhancement of carbon nanofiber emitters via electrical discharge machining," *Appl. Phys. Lett.*, Vol. 90, No. 3, Paper No. 033117, 2007.
8. Kim, B. H., Ok, J. G., Kim, Y. H. and Chu, C. N., "Electrical discharge machining of carbon nanofiber for uniform field emission," *Ann. CIRP*, Vol. 56, No. 1, pp. 233-236, 2007.
9. Ok, J. G., Kim, B. H., Chung, D. K., Sung, W. Y., Lee, S. M., Lee, S. W., Kim, W. J., Park, J. W., Chu, C. N. and Kim, Y. H., "Electrical discharge machining of carbon nanomaterials in air: machining characteristics and the advanced field emission applications," *J. Micromech. Microeng.*, Vol. 18, No. 2, Paper No. 025007, 2008.
10. Zhu, Y. W., Sow, C.-H., Sim, M.-C., Sharma, G. and Kripesh, V., "Scanning localized arc discharge lithography for the

- fabrication of microstructures made of carbon nanotubes,” *Nanotechnology*, Vol. 18, No. 38, Paper No. 385304, 2007.
11. Khalid, W., Mohamed Ali, M. S., Dahmardeh, M., Choi, Y., Yaghoobi, P., Nojeh, A. and Takahata, K., “High-aspect-ratio, free-form patterning of carbon nanotube forests using micro-electro-discharge machining,” *Dia. Rel. Mat.*, Vol. 19, No. 11, pp. 1405-1410, 2010.
 12. Dahmardeh, M., Nojeh, A. and Takahata, K., “Possible mechanism in dry micro-electro-discharge machining of carbon-nanotube forests: A study of the effect of oxygen,” *J. Appl. Phys.*, Vol. 19, No. 9, Paper No. 093308, 2011.
 13. Chung, D. K., Shin, H. S., Park, M. S., Kim, B. H. and Chu, C. N., “Recent researches in micro electrical machining,” *Int. J. Precis. Eng. Manuf.*, Vol. 12, No. 2, pp. 371-380, 2011.
 14. Ok, J. G., “Electrical discharge machining of carbon nanomaterials: a study on the machining characteristics and the advanced field emission applications,” M.S. Thesis, School of Mechanical and Aerospace Engineering, Seoul National University, 2007.
 15. Kunieda, M. and Yoshida, M., “Electrical discharge machining in gas,” *Ann. CIRP*, Vol. 46, No. 1, pp. 143-146, 1997.
 16. Abbas, N. M., Solomon, D. G. and Bahari, M. F., “A review on current research trends in electrical discharge machining (EDM),” *Int. J. Mach. Tools Manuf.*, Vol. 47, No. 7-8, pp. 1214-1228, 2007.