# LETTER

# **Open Access**

# Possibility of large-area carbon nanotube films formation through spray coating



Jinkyeong Kim<sup>1†</sup>, TaeGu Lee<sup>2</sup>, Ji-Hoon Han<sup>3\*†</sup> and Joon Hyub Kim<sup>1\*†</sup>

# Abstract

This study deals with the process of developing and optimizing the spray coating method for large-area deposition of carbon nanotubes. Carbon nanotubes have excellent electrical and thermal properties and strength, so they are used in various fields of application. However, existing deposition methods have limitations. In this study, the possibility of the spray coating method for large-area deposition of carbon nanotubes is presented, and additional conditions for this are introduced. A spray coating solution was prepared using dichlorobenzene as a solvent for 3 mg carbon nanotubes. By controlling the spray coating speed, the spray coating conditions were optimized by analyzing the surface shape, structure, and resistance of the deposited carbon nanotubes. As a result, we confirmed the possibility of depositing carbon nanotubes on a large area through the spray coating method, and it is expected to contribute to increasing the application possibilities in industrial and scientific fields.

Keywords Carbon nanotubes, Spray-coating, Large-area deposition

# Introduction

Semiconductor technology has developed rapidly since semiconductors were first invented in the 1940s and integrated semiconductors were first commercialized in the 1960s. Gordon Moore, a co-founder of Intel and a semiconductor scientist, announced 'Moore's Law,' which states that semiconductor performance doubles every 1 year and 6 months. Over the past 50 years, advances in technology such as miniaturization have resulted in successful commercial products that benefit everyone's daily

 $^\dagger {\rm JinKyeong}$  Kim, JiHoon Han and JoonHyub Kim contributed equally to this work.

\*Correspondence:

Ji-Hoon Han

dafory@inha.ac.ki

Joon Hyub Kim

kim4539@pusan.ac.kr

<sup>1</sup> Department of Nanomechatronics Engineering, Pusan University, 2 Busandaehak-ro 63 beon-gil, Geumjeong-gu, Busan 46241, Republic of Korea

<sup>2</sup> Department of Design, Pusan University, 2 Busandaehak-ro 63 beon-gil, Geumjeong-gu, Busan 46241, Republic of Korea

<sup>3</sup> KIURI Center for Hydrogen Based Next Generation Mechanical System, Inha University, Incheon 22212, Republic of Korea life. For example, Hyundai Microelectronics Co., Ltd. has continuously reduced device size as predicted by Moore's Law [1]. Originating from Hyundai Microelectronics Co., Ltd., the field of micro electromechanical systems (MEMS) has seen continuous development over the past few decades, with mature commercial products such as silicon pressure sensors, micro accelerometers, and micro gyroscopes widely used in automobiles, mobile phones, and video games [2-4].

However, process miniaturization technology is gradually slowing down. For example, a new 14 nm class product that should have been released in 2014 was released in early 2015, and a 10 nm class model that should have been released in 2016 was released in 2017. As a result, an atmosphere was created in the academic world that could no longer keep up with the speed suggested by Moore's Law. Research to overcome this is being conducted concurrently. There are three major research directions. As in the past, the first is to further refine the process, and the second is to improve the design method (architecture) instead of increasing the degree of integration. The third method is to use other materials to replace silicon, the main material of semiconductors.



© The Author(s) 2023. **Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

Of these, new materials such as carbon nanotubes, graphene, molybdenum disulfide, and black phosphorus are noteworthy. Among them, carbon nanotubes are materials that are close to commercialization, as researchers at Stanford University in the US applied carbon nanotube-based transistors to computers in 2013 [5].

Carbon nanotubes have unique electrical, chemical and mechanical properties such as high electrocatalytic activity [6-8], large surface area [9, 10], and ability to mitigate surface contamination [11, 12]. These properties lead to high chemical stability, effective electron transfer, high sensitivity, low detection limit and improved signal-tonoise ratio. Because of these wonderful properties, they have been applied to many devices. Their high conductivity and aspect ratio enable them to deliver high current densities up to  $10^{13}$  A/cm<sup>2</sup> at low voltages. Due to these field-emission characteristics they are used in low-voltage cold-cathode lighting sources, electron microscope sources and lightning arrestors [13]. With their excellent electrical conductivity, extremely high surface area and thermal conductivity, carbon nanotubes are the preferred material for use as electrodes in capacitors and batteries because of their very easy access to electrolytes. Studies have demonstrated that carbon nanotubes have the highest reversible capacity among carbon materials for use in lithium-ion batteries [14]. The anisotropic thermal conductivity of carbon nanotubes is routinely used in electronic products exceeding 100 °C [15]. The biocompatibility of carbon nanotubes demonstrated through several papers and the functionalization of their excellent sidewalls helped them to be applied to biosensors [16, 17].

Furthermore, when existing electronic devices reach their limits, carbon nanotubes offer the possibility of exceeding those limits. The existing devices presented so far had limitations in terms of flexibility and lightness in terms of materials and design. Due to these shortcomings, it has been difficult to break away from the mold of large electronic devices such as existing laptops and smartphones, but carbon nanotubes offer the potential to greatly improve the design of electronic devices due to their flexibility and durability.

There is an increasing demand to develop new viable manufacturing technologies capable of large-area carbon nanotubes at low cost, low temperature, and high throughput while maintaining excellent properties in the device being developed. carbon nanotube large-area technologies such as inkjet printing, gravure printing, screen printing, and microcontact printing have high throughput and are inexpensive, but have poor lateral resolution and electrical properties [18]. Another introduced technique has high lateral resolution, but has the disadvantages of high cost, slow throughput, and difficulty in modifying carbon nanotubes [19]. Among them, carbon nanotube spray coating is a technology that can achieve large-area size in a relatively simple and efficient way. After dispersing carbon nanotubes in a fluid, large-area coverage can be achieved by coating the dispersed nanotubes on a suitable substrate by spraying. This method is relatively simple in process and can be applied to a large area, which is advantageous for mass production.

This paper deals with the stable large-area technology of carbon nanotubes through spray coating. First, the resistance of carbon nanotubes according to the spray coating speed is examined, and the optimal spray coating parameters for this are introduced. It is hoped that the experimental results will provide indicators for new applications or improvement of existing technologies.

#### Materials

Figure 1 shows the process of making a carbon nanotube dispersion solution for spray coating. Carbon nanotubes synthesized by the arc discharge method using iron as a catalyst were purchased from Hanwha Nanotech Co. (Korea). (Containing more than 70 wt% of carbon nanotubes and less than 30% of impurities) 3 mg of purchased carbon nanotubes in 150 mL of dichlorobenzene was tip sonicated for 20 min to obtain a uniform suspension. Then, a uniformly dispersed carbon nanotube solution for spray coating is obtained by ultracentrifugation (20,000 g, 20 min, 4 °C). A 20 mL portion of the supernatant obtained after centrifugation was sprayed on the glass substrate four times in room temperature environment, and simultaneously dried at 190 °C.

#### **Results and discussion**

### Surface and thickness change of carbon nanotubes according to spray coating speed

Figure 2a, the homemade spray coating device. In order to examine the various changes of carbon nanotubes according to the spray coating speed, other spray conditions were fixed, and only the spray rate was varied such as 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1, 2, 5, and 10 mL cm<sup>-2</sup>. Carbon nanotubes were deposited on the target surface while controlling the coating speed, which was confirmed using Atomic Force Microscopes (AFM). As shown in Fig. 2b, it was confirmed that the number of carbon nanotubes coated on the surface increased as the spray coating speed increased. It can be seen that when a velocity of 0.1 mL cm<sup>-2</sup> or higher is secured, the carbon nanotubes form a network-type layer. However, if the velocity is greater than 5 mL cm<sup>-2</sup>, the carbon nanotubes are entangled with each other during the spraying process, making it difficult to form a network surface. It is assumed that this is because too many carbon nanotubes



Fig. 1 Process of making carbon nanotube dispersion solution for spray coating



Spray coating speed

Fig. 2 a The illustrations and b photos of the homemade spray coating device, and c carbon nanotube surface morphology according to spray coating speed using AFM (scan size: 1  $\mu$ m)

are sprayed so that the sprayed carbon nanotubes are uniformly located on the target surface.

Additionally, the carbon nanotube coating thickness according to the spray rate was confirmed through AFM. At each speed, the spray-coated carbon nanotubes were protected with photoresist in a defined area using lithography, and the remaining areas of the carbon nanotubes were etched with a 50 W oxygen plasma treatment for 300 s (Fig. 3a). An AFM scan was performed between the protected and etched areas to determine the carbon nanotube coating thickness according to the spray rate (Fig. 3b), and each data was calculated as an average of 10 samples. As shown in Fig. 3c, the carbon nanotube thicknesses derived from AFM line profiles were about 85 nm at 1 mL cm<sup>-2</sup>, 155 nm at 2 mL cm<sup>-2</sup>, and 350 nm at 5 mL cm<sup>-2</sup>. Carbon nanotubes coated at a rate of  $0.1 \text{ mL cm}^{-2}$  or less were unable to measure the thickness because a perfect film was not formed. And it was impossible to define the thickness of the carbon nanotubes

Positive photoresist

patterning using lithography process

SWCNT

Glass

0

(a)

Carbon nanotube film

ated on a glass

substrate

(b)

(c)

500

400

300

200

coated at a speed of 5 mL  $\rm cm^{-2}$  or more because the film thickness varied greatly due to the entanglement of the carbon nanotubes during the deposition process.

## Change in resistance of carbon nanotubes according to spray coating speed

According to Fig. 3d, a clear relationship was observed between the spray coating rate and the resistance of the carbon nanotubes. The resistance of the coated carbon nanotube film was measured using a digital multimeter (Keysight 34461A) using a 2-point measurement method. To measure only the resistance of carbon nanotubes, palladium electrodes were deposited at 4 mm intervals on the coated carbon nanotubes at each spray speed, and the electrode width was 2 mm. The measured resistance values include line resistance, contact resistance and resistance of the carbon nanotube film. However, since the measurement environment is controlled as much as

Patterned carbon nanotub

Carbon nanotube films

Positive photor

Positive photoresist

develo ent



0000000

Glass wafer

(d)

10M

1M

100K

10K

1K

Oxygen plasma etching

100 75 50

25

75

coating speed

possible, it can be assumed that the line resistance and the contact resistance are the same, and for this reason, there is no problem in confirming the tendency of the resistance change of the carbon nanotubes according to the spray coating speed. As shown in Fig. 2c, d, at low coating rates, the dispersion of the carbon nanotubes was insufficient, leading to uneven coating on the surface, resulting in a relatively high resistivity. On the other hand, at a high coating rate, the carbon nanotubes were excessively stacked, resulting in a large amount of carbon nanotubes on the same surface, which led to a smooth charge flow and reduced resistance. Looking more closely, as the thickness of the carbon nanotube film increased, the carbon nanotube resistance rapidly decreased, followed by a very gradual decrease at t>80 nm. Thinner films exhibited higher resistivity as in previous reports [20].

#### Optimal spray coating speed

Several experimental results were analyzed to determine the optimal coating speed. From the experimental results, it was confirmed that the resistance of the carbon nanotubes decreased as the coating speed increased within a certain range. However, at an excessive coating speed, it tends to be difficult to form a network layer of carbon nanotubes because the stacking of the carbon nanotubes becomes non-uniform. Based on this, when the carbon nanotubes are spray-coated according to the proposed method, it means that a spray speed of 1 mL cm<sup>-2</sup> or more is required to secure a stable resistance value of the carbon nanotube network layer. Furthermore, a spray rate of less than 5 mL cm<sup>-2</sup> is required to obtain a network-type layer. Therefore, the optimal spray coating rate is shown to be 1 or 2 mL cm<sup>-2</sup>.

#### Chemical stability of spray-coated carbon nanotubes

The chemical stability of the carbon nanotube spray coating process was evaluated through X-ray Photoelectron Spectroscopy (XPS) analysis. XPS analysis has been used as a useful tool to investigate the surface chemical composition of carbon nanotubes and the oxidation state of elements. As shown in Fig. 4a, from the results of the C1s



Fig. 4 a C1s deconvolution and b full scale XPS spectra of carbon nanotube deposited by spray coating and other methods

deconvolution analysis, it was observed that the surface chemical composition of the spray-coated carbon nanotubes did not change significantly. As a result of analyzing the full-scale XPS spectra of C1s, O1s, and N1s, there was no significant difference in the peak position and shape of the carbon (C) element, which is the main chemical component of the spray-coated carbon nanotubes, before and after coating (Fig. 4b). This suggests that the chemical stability of the carbon nanotubes was maintained during the spray coating process. XPS analysis was also utilized to determine the presence of oxidized carbon or attached impurities. In the experimental results, almost no change in the characteristic XPS peak of oxygen oxide (O) or other impurities formed on the surface of the spray-coated carbon nanotubes was detected. This suggests that there was little or no oxidation or impurity formation during the spray coating process.

By confirming that the chemical stability of the spraycoated carbon nanotubes was maintained through XPS analysis, it was proved that the coating process proceeded stably without damaging the basic chemical properties of the carbon nanotubes. This emphasizes that it is an important factor that can increase the applicability of carbon nanotubes while performing large-area structuring through spray coating.

#### Conclusion

There is an increasing demand to develop new viable manufacturing technologies capable of large-area carbon nanotubes at low cost, low temperature, and high throughput while maintaining excellent properties in the device being developed. As a result of examining the stable large-area technology of carbon nanotubes through spray coating, it was proved that the proposed technology is suitable for large-area. When spray coating carbon nanotubes according to the proposed method, in order to secure a stable resistance value of the carbon nanotube network layer, a spray rate of 1 mL  $cm^{-2}$  or higher is required. A spray rate of less than 5 mL  $\rm cm^{-2}$ is required. As we have seen, the optimum spray coating rate is shown to be 1 or 2 mL  $cm^{-2}$ . In addition, by confirming that the chemical stability of the spray-coated carbon nanotubes was maintained through XPS analysis, it was proved that the coating process proceeded stably without damaging the basic chemical properties of the carbon nanotubes. It is expected that the experimental results will provide indicators for new application fields or improvement of existing technologies.

#### Acknowledgements

This research is supported Year 2021 Culture Technology R&D Program by Ministry of Culture, Sports and Tourism and Korea Creative Content Agency (Project Name: The expandable Park Platform technology development and demonstration based on Metaverse-Al convergence, Project Number: R2021040269).

#### Author contributions

JHK, J-HH and JKK contributed equally to this work. JHK and J-HH Conceptualized and designed the experimental framework, and conducted SWCNTs etching using  $O_2$  plasma and characterized the modified SWCNT. JKK synthesized SWCNTs and prepared the  $O_2$  plasma treatment setup, and investigated the effects of  $O_2$  plasma on SWCNTs surface properties. JHK, J-HH and JKK Co-authored the introduction, methodology section, and analyzed the data from the spray deposition experiments and Co-wrote discussion sections of the manuscript. TGL assisted in experimental setup design, particularly in the spray deposition process, and supported the data collection and analysis of SWCNTs properties after spray deposition.

#### The authors declares that they have no funding.

Funding

#### Availability of data and materials

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

#### Declarations

**Ethics approval and consent to participate** Not applicable.

#### **Consent for publication**

Not applicable.

#### **Competing interests**

The authors declares that they have no competing interests.

Received: 17 August 2023 Accepted: 14 December 2023 Published online: 04 March 2024

#### References

- Wu J, Shen YL, Reinhardt K, Szu H, Dong B (2013) A nanotechnology enhancement to Moore's law. Appl Comput Intell Soft Comput. https:// doi.org/10.1155/2013/426962
- Wang Z, Xiong XY, Wang KF, Yang WH, Wang BW, Li ZT, Zou XD (2023) Utilizing mechanical micro-lever coupling structure to enhance sensitivity in mode-localized MEMS accelerometer. Sens Actuators A Phys 351:114172
- Han JH, Min SJ, Kim JH, Min NK (2023) Reciprocating arc silicon strain gauges. Sensors 23:1381
- KomarizadehaslS Komary M, Alahmad A, Lozano-Galant JA, Ramos G, Turmo J (2022) A NovelWireless low-cost inclinometer made from combining the measurements of multipleMEMS gyroscopes and accelerometers. Sensors 22:5605
- Yao X, Zhang Y, Jin W, Hu Y, Cui Y (2021) Carbon Nanotube field-effect transistor-based chemical and biological sensors. Sensors 21(3):995
- Carroll DL, Redlich P, Ajayan PM, Charlier JC, Blase X, De Vita A, Car R (1997) Electronic structure and localized states at carbon nanotube tips. Phys Rev Lett 78(14):2811
- Wong EW, Sheehan PE, Lieber CM (1997) Nanobeam mechanics: elasticity, strength, and toughness of nanorods and nanotubes. Science 277(5334):1971–1975
- Wang Z, Liu J, Liang Q, Wang Y, Luo G (2002) Carbon nanotube-modified electrodes for the simultaneous determination of dopamine and ascorbic acid. Analyst 127:653–658
- Cahill PA, Rohlfing CM (1996) Theoretical studies of derivatized buckyballs and buckytubes. Tetrahedron 52(14):5247–5256
- Musameh M, Wang J, Merkoci A, Lin Y (2002) Low-potential stable NADH detection at carbon-nanotube-modified glassy carbon electrodes. Electrochem Commun 4(10):743–746
- 11. Wang J, Li M, Shi Z, Li N, Gu Z (2002) Direct electrochemistry of cytochrome c at a glassy carbon electrode modified with single-wall carbon nanotubes. Anal Chem 74:1993–1997

- Wang J, Musameh M, Lin Y (2003) Solubilization of carbon nanotubes by Nafion toward the preparation of amperometric biosensors. J Am Chem Soc 125:2408–2409
- 13. Wei BQ, Vajtai R, Ajayan PM (2001) Reliability and current carrying capacity of carbon nanotubes. Appl Phys Lett 79:1172–1174
- Gao B, Bower C, Lorentzen JD, Fleming L, Kleinhammes A, Tang XP, Mcneil LE, Wu Y, Zhou O (2000) Enhanced saturation lithium composition in ballmilled single-walled carbon nanotubes. Chem Phys Lett 327(1–2):69–75
- Lin M, Zheng Z, Yang L, Luo M, Fu L, Lin B, Xu C (2022) A high-performance, sensitive, wearable multifunctional sensor based on rubber/ CNT for human motion and skin temperature detection. Adv Mater 34(1):2107309
- Kim J, Park G, Lee S, Hwang SW, Min N, Lee KM (2017) Single wall carbon nanotube electrode system capable of quantitative detection of CD4+T cells. Biosens Bioelectron 90:238–244
- Shao K, Zhang C, Ye S, Cai K, Wu L, Wang B, Zou C, Lu Z, Han H (2017) Near–infrared electrochemiluminesence biosensor for high sensitive detection of porcine reproductive and respiratory syndrome virus based on cyclodextrin-grafted porous Au/PtAu nanotube. Sens Actuators B 240:586–594
- Pandhi T, Chandnani A, Subbaraman H, Estrada D (2020) A review of inkjet printed graphene and carbon nanotubes based gas sensors. Sensors 7(8):3338–3355
- Choi HW, Zhou T, Singh M, Jabbour GE (2015) Recent developments and directions in printed nanomaterials. Nanoscale 7(8):3338–3355
- Doherty EM, De S, Lyons PE, Shmeliov A, Nirmalraj PN, Scardaci V, Joimel J, Blau WJ, Boland JJ, Coleman JN (2009) The spatial uniformity and electromechanical stability of transparent, conductive films of single walled nanotubes. Carbon 47:2466–2473

#### **Publisher's Note**

Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

# Submit your manuscript to a SpringerOpen<sup>™</sup> journal and benefit from:

- Convenient online submission
- ► Rigorous peer review
- Open access: articles freely available online
- ► High visibility within the field
- Retaining the copyright to your article

Submit your next manuscript at > springeropen.com