Evaluation of Thin Film Surface Shape as a Function of Dispersant Concentration in Carbon Nanotube Thin Film Fabrication via the Electrospray Method*

Yongil Kim† and Eiichi Nishikawa
Department of Electrical Engineering, Tokyo University of Science, 6-3-1 Niiyuku, Katsushika, Tokyo 125-8585, Japan

Yasuyuki Watanabe
Department of Electrical and Electronic Engineering, Suwa University of Science, 5000-1 Toyohira, Chino-City, Nagano 391-0292, Japan
(Received 9 January 2018; Accepted 5 May 2018; Published 21 June 2018)

Electrospray deposition (ESD) is a method of producing a variety of thin films, and is widely employed for industrial-use electrostatic coatings, such as automotive paint. In ESD, the electrospray phenomenon is utilized to produce nanothin films using a simple device configuration. In this study, we fabricated carbon nanotube (CNT) thin films via ESD, using a multi-walled nanotube solution. We found that irregularities formed on the thin film surface because the surfactant crystallized. However, the CNT thin film, for which sodium dodecyl sulfate (SDS) was not used, exhibited a uniform thickness. [DOI: 10.1380/ejssnt.2018.302]

Keywords: Carbon nanotubes; Electrospray deposition; Surfactant; Thin films

I. INTRODUCTION

At present, indium tin oxide (ITO) is widely used for the main transparent electrode films in liquid crystal display panels and solar batteries made of organic electroluminescent materials, touch panels, flat panel displays, and so on [1–6]. However, indium, which is a rare metal, is expensive, and its supply is limited. Furthermore, ITO film is fragile and lacks flexibility. Carbon nanotubes (CNTs) are expected to serve as a substitute for indium as a flexible and transparent conducting material.

CNTs are new allotropes of carbon that were discovered by Dr. Sumio Iijima in 1991 [7]. They have a variety of advantages such as lightness, flexibility, high strength, and high conductivity, due to the manner in which the graphite sheets, which have carbon atoms arranged in a hexagon pattern, are wound and overlapped. Consequently, they are expected to have applications not only in biotechnology, but also as next-generation electrode materials [8–11].

Meanwhile, because ITO thin films are generally manufactured via sputtering, which requires vacuum equipment and involves high costs, a simple and low-cost film fabrication method is called for. Electrospray deposition (ESD), which is one type of thin film manufacturing method, is widely employed for industrial-use electrostatic coatings, such as those applied to automobiles, and it is advantageous since it can be performed using a simple device configuration [12–19].

In this study, we produced CNT thin films [multi-walled nanotube (MWNT) thin film] via ESD. Furthermore, we fabricated CNT thin films using two types of MWNT solutions, one with and one without a surfactant. By analyzing the surface shape differences between the CNT thin films, we attempted to produce CNT thin films that could serve as transparent conducting materials suitable for ESD.

II. EXPERIMENTAL

In ESD, the solution that will become the thin film is sprayed onto the substrate. As shown in Fig. 1, ESD is based on the principle that charged solution droplets are ejected in the form of a spray when a high voltage (of the order of a few kV) is applied to a solution. Due to the electric field concentration resulting from the application of a high voltage to the sharp tip of a container, droplets that are positively charged by the high voltage spread in space as they repeatedly break down into smaller ones due to the Coulomb repulsions among droplets. The sprayed solution is deposited on the substrate by the electrostatic force and forms a thin film, making it possible to fabricate thin films for a variety of applications by controlling the deposited patterns using masking and auxiliary electrodes. Therefore, it is possible to fabricate a second organic layer without melting the underlying organic layer, which is necessary in evaporation methods.

* This paper was presented at the 8th International Symposium on Surface Science, Tsukuba International Congress Center, Tsukuba, Japan, October 22-26, 2017.
† Corresponding author: kim@rs.tus.ac.jp

FIG. 1. Schematic of the principle of ESD
A. Experimental method

As shown in the experimental setup in Fig. 2, the experimental device consists of a container (pipette) for storing the thin film solution, a sharp needle (capillary) at the tip of the pipette, and a direct current power source to apply a high voltage between the capillary and substrate. Due to the electric field concentration resulting from applying a high voltage to the sharp tip, a strong electric field is generated. The charged droplets inside the pipette spray out due to the breaking of the surface tension. The sprayed solution is deposited on the substrate by the electrostatic force and becomes a thin film. By controlling the deposited patterns by masking or auxiliary electrodes, it is possible to fabricate thin films for a variety of applications.

1. To produce the capillary used in the experiments, we applied heat to one end of a glass tube and stretched it out very thin, then cut the tip to the desired diameter. This procedure yielded a glass capillary with a bore diameter of approximately 0.12–0.15 mm.

2. We fitted the capillary to the tip of the glass pipette and filled the pipette with MWNT solution, as shown below. To apply a high voltage to the MWNT solution, we placed a linear negative electrode inside the glass pipette and mounted a positive electrode on the glass substrate.

3. We gradually increased the direct current voltage while maintaining a distance of 100 mm between the capillary tip and substrate surface. When the voltage exceeded 10 kV, CNT solution sprayed from the tip of the capillary, and MWNTs were deposited on the substrate surface.

B. MWNT solutions (with or without dispersant)

In general, CNTs [MWNTs and single-walled nanotubes (SWNTs)] aggregate due to van der Waals forces, so it is necessary to disperse CNTs into solutions using surfactants. Sodium dodecyl sulfate (SDS) is a white crystalline powder and a representative anionic surfactant commonly used as the main agent in neutral clothing detergents, kitchen detergents, and shampoos. In addition to being used as an emulsifier in medicines and cosmetics, it is widely used in industrial applications as a surfactant in emulsion polymerization and scouring detergent for fibers.

In particular, in single-walled carbon nanotubes (SWNTs), as all constituent atoms are surface atoms, aggregation due to van der Waals forces between adjacent CNTs occurs frequently, leading to the formation of bundle structures composed of several CNTs. This high cohesiveness is the greatest barrier to the chemical and physical manipulation of CNTs and their industrial use. To solve this issue, various dispersion methods for obtaining isolated and dispersed CNTs have been proposed. For example, to isolate and disperse CNTs in solution, physical dispersion processes, such as ultrasonic treatment, have been proposed. In addition to ultrasonic treatment, adding a surfactant to the solvent to cover the CNTs has been shown to increase the solvent affinity (particularly hydrophilicity) of CNTs. The surfactants used are diverse, but it has been reported that by placing CNT aggregates in an aqueous solution of SDS, the hydrophilicity of the hydrophobic CNT surface can be increased. Thus, the dispersion due to ultrasonic treatment becomes more effective [20–25].

Therefore, we employed two types of MWNT sample solutions, one with SDS and one without.

1. To produce the first thin film, sample 1, we used MWNTs (Meijo Nano Carbon Co., Ltd. MWNT INK: 100 mL (MWNT: 2 wt%, H$_2$O) (see Table I) dispersed in SDS, which was mixed with 100 mL of distilled water at a 0.1 wt% concentration to produce an MWNT solution.

2. To fabricate the second thin film, sample 2, we used an MWNT solution made of MWNTs (MW-I MWNT INK: 100 mL) dispersed in 100 mL of distilled water.

3. To obtain the MWNT solutions for ESD, we dispersed each of the samples using an ultrasonic cleaning machine (FU-2H, oscillating frequency 38 kHz) for 1 h.

C. CNT thin film evaluation methods

We employed the following three methods to evaluate the CNT thin films produced via ESD.

1. We observed the surface of each thin film using a CS5110C (optical microscope at 2$\times$ magnification) and also investigated the thickness uniformity of the

| TABLE I. Description of CNTs. |
|-------------------------------|
| Model | MW-1 |
| Type  | MWNT |
| Diameter | 10–40 nm |
| Solvent | H$_2$O |
| Density of CNT | 2 wt% |
| Carbonic purity | 90% or more |
| CNT diameter | Approximately 10 nm |
thin film using a surface shape measuring instrument (Surfcorder ET 4000A).

2. We employed a scanning electron microscope (SEM) to observe the CNT thin film MWNTs.

III. RESULTS AND DISCUSSIONS

The data obtained using the CNT thin films fabricated in this study are presented below.

A. Evaluation of sample surfaces using optical microscope images

Figures 3(a) and 3(b) present optical microscope images of the surfaces of samples 1 and 3, respectively. Figure 3(a) shows the surface of sample 1 observed through an optical microscope. Figure 3(b) shows the surface of sample 2 observed through an optical microscope.

The average thicknesses of samples 1 and 2, which were produced with and without SDS, were measured to be 28.2 μm and 8.80 μm, respectively. Thus, using SDS made the thin film thicker. Furthermore, in Fig. 3(a), which depicts the sample fabricated using SDS, white specks that appear to be SDS crystals are marked by rectangles. In the film thickness mapping results as well, parts can be seen that project out sharply. The amount of SDS used in the MWNT solution was 1.0 wt%. We believe that if more SDS was used, even more SDS crystals would appear on the surface of the thin film.

B. Evaluation of sample surfaces using Surfcorder images

Figures 4(a) and 4(b) present the asperities of the thin film surfaces of samples 1 and 2, respectively, measured using the Surfcorder.

Figure 4(a) reveals asperity of approximately 28.2 μm on the surface of sample 1, which we believe was caused by surfactant crystals precipitating on the surface. The film was found to be 28.2 μm thick, thicker than sample 2. We believe that the increase in film thickness is due to the hardening of the surfactant, rather than the CNTs.

As shown in Fig. 4(b), we observed a maximum asperity of 1 μm on the surface of sample 2, but compared to sample 1, the overall surface shape was flat.

C. SEM images of thin film surfaces

In Fig. 5, numerous pieces of particulate matter are evident on the surface of sample 1. The enlarged images in Fig. 5(b–d) reveal CNTs stuck to the surface of the particulate matter. The diameter of the particulate matter ranges from 5 μm to 20 μm, which is about the same as the asperity height measured using the Surfcorder. The surface of sample 2 in Fig. 6(a) is relatively flat compared with that of sample 1. Figures 6(b–d) are enlargements of the marked section of Fig. 6(a), and CNTs are evident.
FIG. 6. (a) Electron microscope image of the thin film surface of sample 2 and (b)–(d) enlargements of the image in (a).

in Fig. 6(c, d) as linear substances ranging from 10 nm to 20 nm in diameter. These images indicate that the CNTs were highly densely intertwined and formed into bundles in the film.

IV. CONCLUSION

In this study, we produced CNT thin film via ESD, and we compared the differences in surface shape of CNT thin films produced with and without SDS in the MWNT solution.

Thus, it is clear that even with a constant duration of spraying and concentration of CNTs, the resulting film becomes thicker with the use of SDS. This is likely due to the retention of SDS after spraying, which significantly impacts the film thickness.

In addition, we found that irregularities formed on the thin film surface because the surfactant crystallized. Therefore, it is preferable not to use SDS when fabricating CNT thin film using MWNT solution; however, if SDS is not used, dispersion of the MWNT solution requires more time. Furthermore, the more time elapses, the more the MWNTs settle in the MWNT solution, so it is necessary to employ a dispersion process during film fabrication.

In future studies, it would be advantageous to search for a dispersant that does not decrease conductivity and to produce CNT solutions using this dispersant instead of a surfactant.

[1] B. Wei, S. Yamamoto, M. Ichikawa, C. Li, T. Fukuda, and Y. Taniguchi, Semicond. Sci. Technol. 22, 788 (2007).
[2] R. Bathelt, D. Buchhauser, C. Grarditz, R. Patetzold, and P. Wellmann, Org. Electron. 8, 293 (2007).
[3] H. Kawaguchi, S. Iba, Y. Kato, T. Sekitani, T. Someya, and T. Sakurai, IEEE Sens. J. 6, 1209 (2006).
[4] M. Hiramoto, H. Fujiwara, and M. Yokoyama, J. Appl. Phys. 72, 3781 (1992).
[5] T. Fukuda, M. Komoriya, R. Kobayashi, Y. Ishimaru, and N. Kamata, Jpn. J. Appl. Phys. 48, 04C162 (2009).
[6] T. Suzuki, T. Fukuda, Z. Honda, and N. Kamata, Thin Solid Films 518, 575, (2009).
[7] S. Iijima, Nature 354, 56 (1991).
[8] J. Kong, H. T. Soh, A. M. Cassell, C. F. Quate, and H. Dai, Nature 395, 878 (1998).
[9] J. Hone, M. C. Liaguno, M. J. Biercuk, A. T. Johnson, B. Batlogg, Z. Benes, and J. E. Fischer, Appl. Phys. A 74, 339 (2002).
[10] J. A. Misewich, R. Martel, P. Avouris, J. C. Tsuang, S. Heinz, and J. Tersoff, Science 300, 783 (2003).
[11] H. Nishijima, S. Kamo, S. Akita, and Y. Nakayama, Appl. Phys. Lett. 74, 4061 (1999).
[12] A. Van Zomeren, E. M. Kelder, J. C. M. Marijnissen, and J. Schoonman, J. Aerosol. Sci. 25, 1229 (1994).
[13] T. Fukuda, M. Ohashi, B. Wei, T. Okada, M. Ichikawa, and Y. Taniguchi, Appl. Opt. Lett. 32, 1150 (2007).
[14] T. Fukuda, T. Okada, B. Wei, M. Ichikawa, and Y. Taniguchi, Appl. Phys. Lett. 90, 231105 (2007).
[15] T. Fukuda, T. Okada, B. Wei, M. Ichikawa, and Y. Taniguchi, Opt. Lett. 32, 1905 (2007).
[16] T. Fukuda, B. Wei, E. Suto, M. Ichikawa, and Y. Taniguchi, Phys. Status Solidi RRL 2, 290 (2008).
[17] T. Suzuki, T. Fukuda, Z. Honda, and N. Kamata, Thin Solid Films 518, 575 (2009).
[18] N. Hu, Y. Karube, C. Yan, Z. Masuda, and H. Fukunaga, Acta Mater. 56, 2929 (2008).
[19] T. Hirata, K. Takagi, and M. Akiya, Jpn. J. Appl. Phys. 46, 2401 (2007).
[20] R. R. Tummala and A. Striolo, ACS Nano 3, 595 (2009).
[21] W. H. Duan, Q. Wang, and F. Collins, Chem. Sci. 2, 1407 (2011).
[22] L. Vaisman, H. D. Wagner, and G. Marom, Adv. Colloid Interface Sci. 128–130, 37 (2006).
[23] M. F. Islam, E. Rojas, D. M. Bergey, A. T. Johnson, and A. G. Yodh, Nano Lett. 3, 269 (2003).
[24] K. Yurekli, C. A. Mitchell, and R. Krishnamoorti, J. Am. Chem. Soc. 126, 9902 (2004).
[25] L. Jiang, L. Gao, and J. Sun, J. Colloid Interface Sci. 260, 89 (2003).