Study of high-mobility thin films containing highly crystalline single-walled carbon nanotubes

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Abstract**—** *While data from various devices as Internet of Things (IoT) are scattered and isolated as silos at present, some expect that hundreds of billions of devices will be connected through the Internet by the early 2020s. To prevent radio interference of huge amounts of data, it is necessary to develop ubiquitous wearable devices that enable constant retention and sharing of data. We aim to establish the basic packaging technology for realizing the semiconductive thin films and circuits that make up such electronic devices, and we fabricated thin films using highly crystalline single-walled carbon nanotubes (HC-SWCNTs) by a wet-coating process and evaluated their electrical properties in this study. Our research has developed a technology to disperse HC-SWCNTs without impairing their crystallinity and succeeded in fabricating thin films from a dispersion liquid of HC-SWCNTs obtained by this technology. We also evaluated the Hall mobility of these thin films and found that a high Hall mobility of 1,000 cm2/Vs can be achieved by controlling the crystallinity. On the basis of the results of this study, we will pursue our research to establish a technology for packaging electronic circuits that take full advantage of the electronic properties of HC-SWCNTs by a wet-coating process.*

Keywords**— single-walled carbon nanotube, high crystallization, IoT, Hall mobility, thin film.**

I. INTRODUCTION

As more electronic devices around us become compatible with the Internet of Things (IoT), networks are being constructed to share information among various devices. While data from various devices are scattered and isolated as silos at present, some expect that hundreds of billions of devices will be connected through the Internet by the early 2020s. Although huge amounts of data and information are constantly generated, they cannot be shared as long as they are isolated as silos. To deal with this issue, it is necessary to develop wearable devices that enable constant retention and sharing of data [1]. Namely, it is desirable to realize wearable electronic devices having nonconventional functions [2-4], such as flexibility that renders them foldable or windable, a light weight, conformability to irregular surfaces [5-7], and comfort while wearing as well as a large area and transparency [8, 9].

Taking advantage of the high Hall mobility that is theoretically expected of highly crystalline single-walled carbon nanotubes (HC-SWCNTs)[10-14], we aim to establish the basic packaging technology for energy-efficient wearable devices that are capable of a high-frequency response with almost zero energy loss. With the aim of realizing a low-carbon and energy-efficient process for the basic performance elements (semiconductive thin films and circuits) that make up devices, we fabricated thin films using HC-SWCNTs by a wet-coating process [15, 16] and evaluated their electrical properties in this study. The SWCNTs used in this study have high potential for use as a semiconductor and have been studied for applications to thin-film transistors (TFTs) for displays [17-20], integrated circuit (IC) tags [21-24], and sensors [25-28] in the field of conventional applied research and development. SWCNTs consist of 60–80% semiconductor tubes and 20–40% metal tubes [29], but the technologies to take advantage of their excellent semiconductor properties have not yet been established. In this study, we attempted to fabricate thin films by supporting SWCNTs on a matrix of indium tin oxide (ITO) so that the SWCNTs act as conductive paths in the thin films.

Although metal oxide films have conventionally been used as materials for electronic elements [31, 32] such as thin-film transistors and display devices, metal oxide films with a higher mobility are required in order to improve the performance of electronic elements and display devices. The results of past research have not satisfied this requirement for metal oxide films. Also, the mobility in metal oxide–carbon composite thin films has remained unclarified. The purpose of this study was to fabricate high-mobility thin films containing HC-SWCNTs by a wet-coating process while suppressing the amount of HC-SWCNTs added. Another aim was to devise a simple technique for fabricating semiconductive thin films with high mobility using fewer HC-SWCNTs under atmospheric pressure.

II. EXPERIMENTAL

2.1 Synthesis of metal oxides

The semiconductive films used in this study consist mainly of ITO as the metal oxide and contain a small amount of carbon nanotubes (CNTs). In ITO, tin oxide is a solid solute in indium oxide and its composition varies with the manufacturing conditions [15, 33, 34]. Some organic components may remain when a metalorganic compound is used as the starting material and the sintering temperature is low; however, the ITO contents in this study represent the values obtained assuming that the indium and tin contained in the field electron emission films are oxides of stoichiometric composition [16, 35].

The semiconductive films fabricated in this study essentially consist of indium oxide, tin oxide, partial decomposition products of organic compounds associated with the raw materials (indium and tin), organic substances derived from the raw materials, and HC-SWCNTs. The conducting films can contain conductive materials, such as metal particles, that do not cause adverse effects on the properties of conductive films fabricated from the materials listed above. However, fundamentally, these films do not contain insulating materials because such materials decrease the conductivity of the films.

The semiconductive films in this study are formed on a Ta substrate using SWCNTs (whose content is controlled within the range of 0.1–20 wt%) as the conductive material. While there is no limit to the type of substrate, a conductive substrate is preferable because such a substrate provides a higher degree of freedom in terms of electrical connections. Thin films with homogeneously dispersed SWCNTs are obtained by coating the substrate with a dispersion liquid, which consists of a material containing indium and a material containing tin, which are precursors of ITO, and CNTs, that forms a wet film coating on the substrate by spray coating, spin coating, dip coating, or any other generally used method, and then heating and sintering the wet film coating to form a CNT-containing ITO film. Thin films mainly consisting of ITO and containing a small amount of SWCNTs can be obtained by heating (sintering) the above-mentioned wet film coating at 430 °C. The sintering is performed in a low-vacuum atmosphere of about 0.1 Pa.

Arc-SWCNTs (ASP-100F; Hanwha Chemicals Co. Ltd., Korea) are used in this study. Highly crystalline SWCNTs are obtained by annealing the SWCNTs at a high temperature (973 K) under a high vacuum (pressure >10^{-4} Pa).

2.2 Initial dispersion liquid

A mixture of 0.01 g of the above-mentioned HC-SWCNTs, ~30 g of ethyl cellulose (48–49.5%, ethoxy 100 cP; Kanto Chemical Co., Inc.), and ~160 g of butyl acetate is prepared. This mixture is subjected to ultrasonic dispersion for 30 min. After the ultrasonic dispersion, the mixture is processed ten times to disperse and collide with ink droplets including HC-SWCNTs and micro-scaled media beads by a jet mill (HJP-25001; Sugino Machine Limited) at a discharge pressure of 60 MPa to obtain a homogeneous dispersion liquid of SWCNTs.

A mixture of the above-mentioned dispersion liquid of SWCNTs and ethyl cellulose (48–49.5%, ethoxy 100 cP; Kanto Chemical Co., Inc.) is prepared. The obtained mixture is then mixed with ~15 mL (17.45 g) of ITO-05C (ITO dipping material; Kojundo Chemical Laboratory Co., Ltd.) and subjected to ultrasonic dispersion for 30 min. After the ultrasonic dispersion, the mixture is processed several times using a jet mill (HJP-25001) at a discharge pressure of 60 MPa to obtain the dispersion liquid used as the starting material. The mass of the ITO film obtained by applying and sintering ITO-05C is 2–3% of that of the ITO-05C.

2.3 SWCNT-containing ITO films

The surface of a 0.1-mm-thick Ta substrate (tantalum plate) is coated with the above-mentioned dispersion liquid of SWCNTs using a static coating spray. The thickness of the film coating is adjusted so that the film thickness after sintering becomes 20 μm. The Ta substrate coated with the dispersion liquid of SWCNTs is heated and dried at 230 °C in air for 30 min. After that, the Ta substrate coated with the dried dispersion liquid of SWCNTs is heated to 470 °C under reduced pressure (0.001 Pa) for 90 min and then left to stand for 30 min to form an SWCNT-containing ITO film on the Ta substrate. Also, SWCNT-containing ITO films that are to be used as a reference are formed on a Ta substrate by the method described above using SWCNTs that are not annealed (not processed at 973 K in a vacuum for 3 h).

Figure 1 shows a transmission electron microscopy (TEM; HR-3000; Hitachi High Tech. Co., Ltd., Japan) image of SWCNTs annealed to achieve high crystallinity and that of nonannealed SWCNTs, showing the difference in crystallinity between them. Nanobubble-like crystalline discontinuities are observed in the wall of the nonannealed SWCNTs [36, 37], indicating that there is a difference in crystallinity between the annealed and nonannealed SWCNTs.

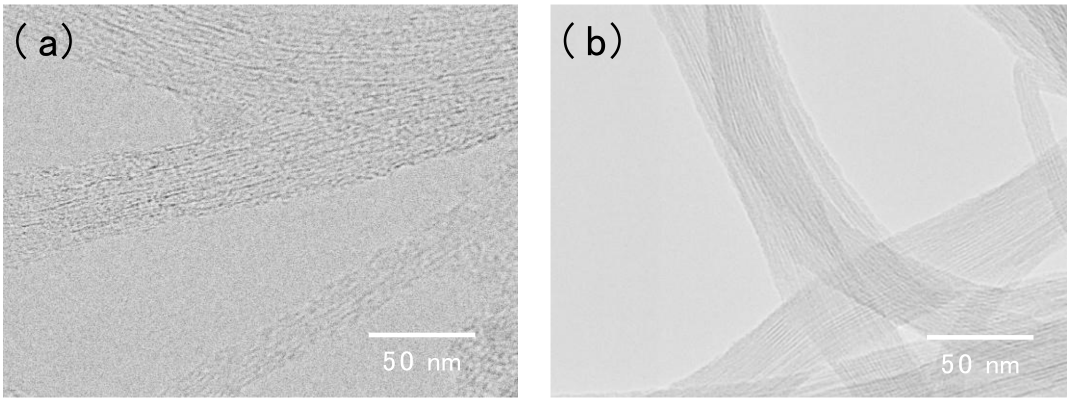

FIG. 1: TEM images of SWCNTs (accelerating voltage, 200 kV).
(a) Commercial SWCNTs and (b) highly crystalline SWCNTs

III. RESULTS AND DISCUSSION

3.1 Evaluation of film coating

The amount of SWCNTs added to thin films is controlled arbitrarily in this study. Figure 2 shows thin films containing controlled amounts of highly crystalline HC-SWCNTs. The density of HC-SWCNTs added to the thin films is defined as the weight of added HC-SWCNTs per unit area (weight density).

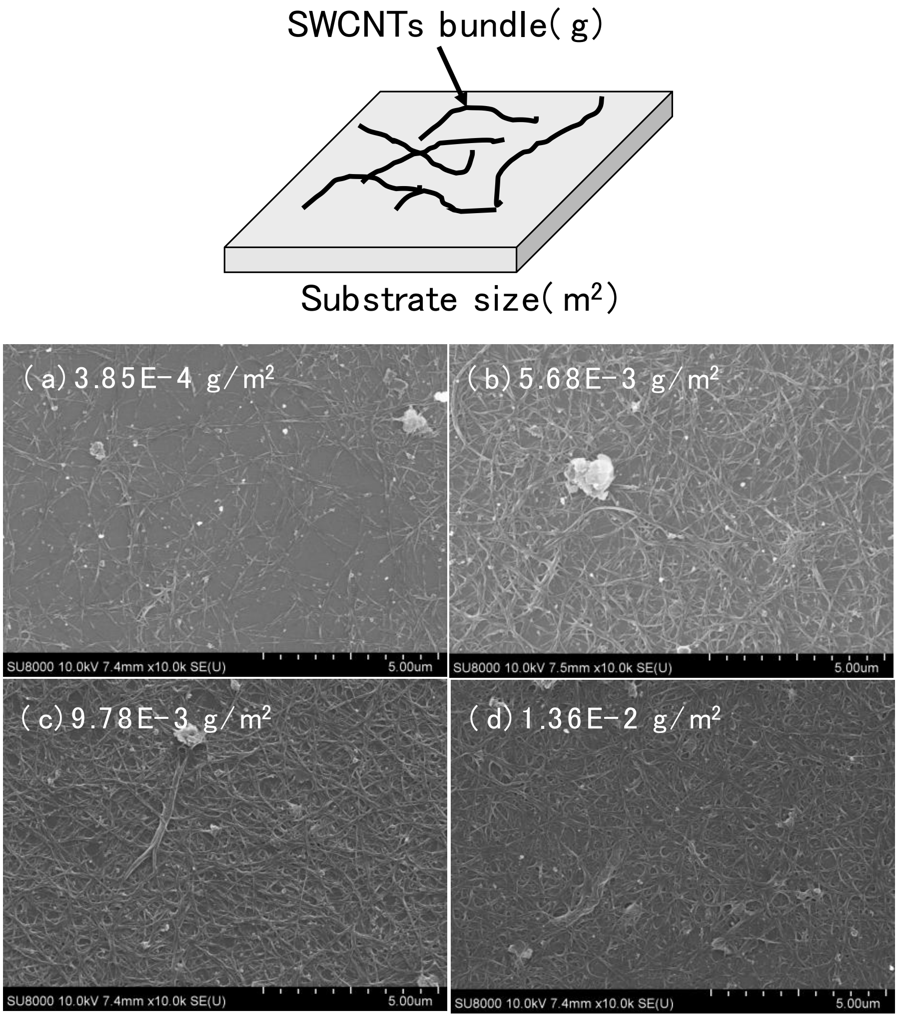

FIG. 2: Schematic of definition of weight density (top) and SEM images of surface of thin films containing HC-SWCNTs at controlled weight densities (bottom).
(a) 3.85×10^{-4} g/m^2, (b) 5.68×10^{-3} g/m^2, (c) 9.78×10^{-3} g/m^2, and (d) 1.36×10^{-2} g/m^2.

The dispersion state of SWCNTs with crystal defects is similar to that of HC-SWCNTs. Scanning electron microscopy (SEM) images show no difference in the appearance of dispersion states among SWCNTs with different crystallinity.

3.2 Measurement of mobility of SWCNT-containing ITO films

The Hall mobility of SWCNT-containing ITO films is obtained by the time-of-flight (TOF) method [38-40]. In this method, the thin films to be measured are irradiated with visible light and the time-dependent responsiveness of electric current flowing through the thin films is measured. Figure 3 shows a schematic of the measurement. In this study, thin films are irradiated with pulsed light for an arbitrarily controlled irradiation time and the responsiveness of electric current flowing after the irradiation is analyzed using an oscilloscope. On the basis of the time taken for electrons (current) generated in a thin film to reach the counter electrode [*t* (s)], the distance between the electrodes [*L* (cm)], and the electric field applied to the thin film (V/cm), the charge-transfer rate per unit electric field and per unit time μ is given by the following Eq. (1). Table 1 shows the conditions for the measurement of mobility.

$$M = L/[t \times (V/L)](\mathrm{cm}^2/\mathrm{Vs}) \quad (1)$$

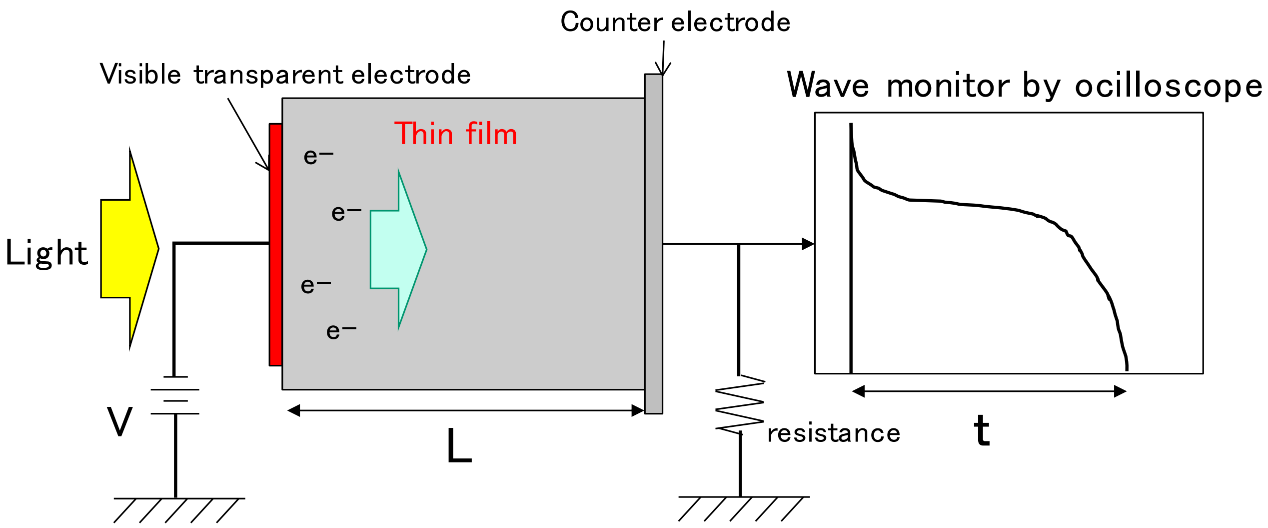

FIG. 3: Evaluation of Hall mobility by TOF method

The oscilloscope used for the measurement is a 3000T X-Series oscilloscope (1 GHz; Keysight Technologies).

TABLE 1
CONDITIONS FOR MOBILITY MEASUREMENT

Measurement sample size	10 mm × 10 mm × 20 μm
Visible transparent electrode	ITO film formed by sputtering method
Counter electrode	Ta substrate
Region formed between visible transparent electrode and counter electrode	$10 \times 10\ \mathrm{mm}^2$
Excitation light source	Halogen lamp
Applied voltage	100 V (DC)

Figure 4 shows the obtained Hall mobilities of thin films containing HC-SWCNTs at arbitrary controlled weight densities. The Hall mobility of ITO films alone and that of the thin films containing SWCNTs with crystal defects at arbitrary controlled weight densities are also measured as references. The results show that the Hall mobility increases as the weight density of SWCNTs increases. The highest Hall mobility of 1,000 cm^2/Vs is achieved in the thin film containing HC-SWCNTs at a weight density of about 1.2×10^{-2} g/m^2. In addition, the Hall mobility varies considerably with the crystallinity; namely, it decreases to one-tenth owing to the presence of crystal defects. The Hall mobility is dependent on the crystallinity of the SWCNTs.

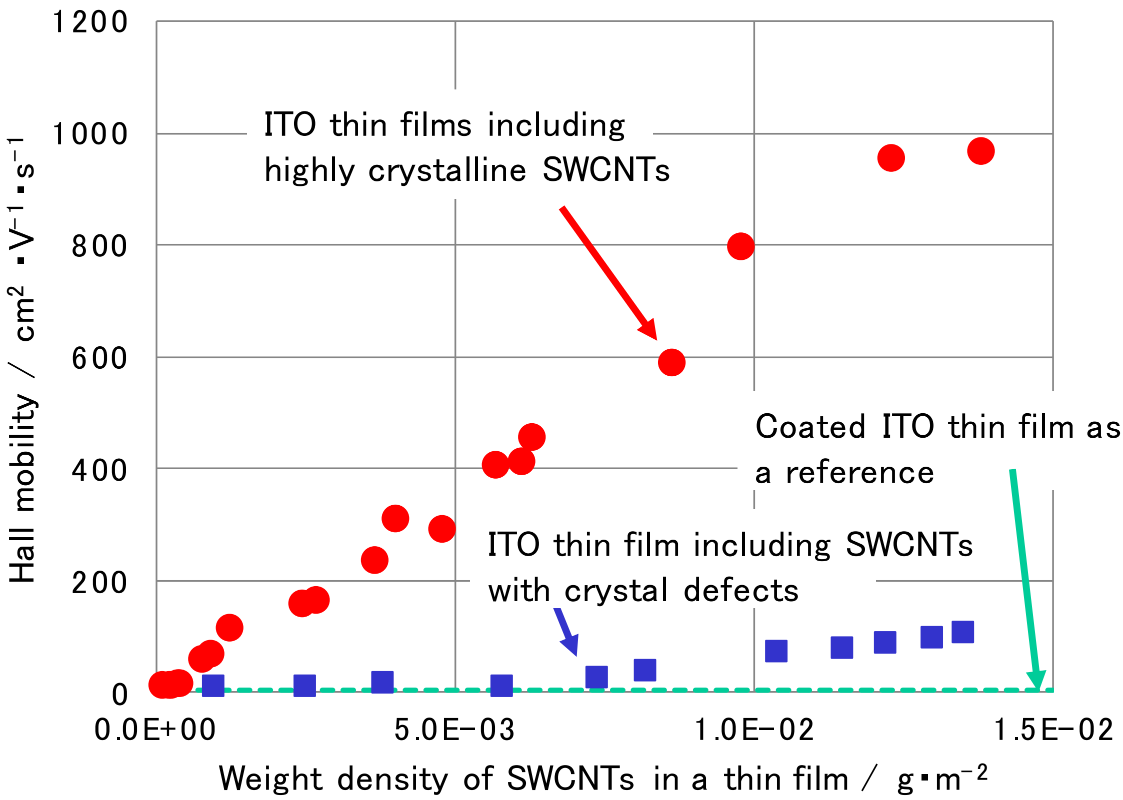

FIG. 4 Dependence of Hall mobility on weight density for different crystallinities of SWCNTs

It is known that CNTs, including SWCNTs, have a high theoretical mobility of 5,000–10,000 cm^2/Vs [41, 42]. In the CNT-containing films formed by a coating method, however, there is electrical resistance at contact points among the CNTs because many CNTs are arranged in a netlike pattern, as shown in Fig. 1. By reducing the electrical resistance among CNTs, their high potential can be realized in applications. Therefore, a variety of research and development projects related to CNT structure formation and control at the nanometer (one-millionth of a millimeter) scale have been carried out, aiming at obtaining CNTs with a small range of variation in diameter. To discuss the mobility shown in Fig. 4, we evaluate the significant variation in contact resistance resulting from the difference in the crystallinity of SWCNTs [43-46]. Nanotubes are dispersed on a Ta substrate and their contact resistance is evaluated using a tunneling current detection scanning probe microscope [SPM; MultiMode8 PeakForce TUNA (tunneling AFM); Bruker Japan K.K.]. An arbitrary voltage is applied between the sample and the probe and the current flowing in the measurement circuit shown in Fig. 5 is obtained.

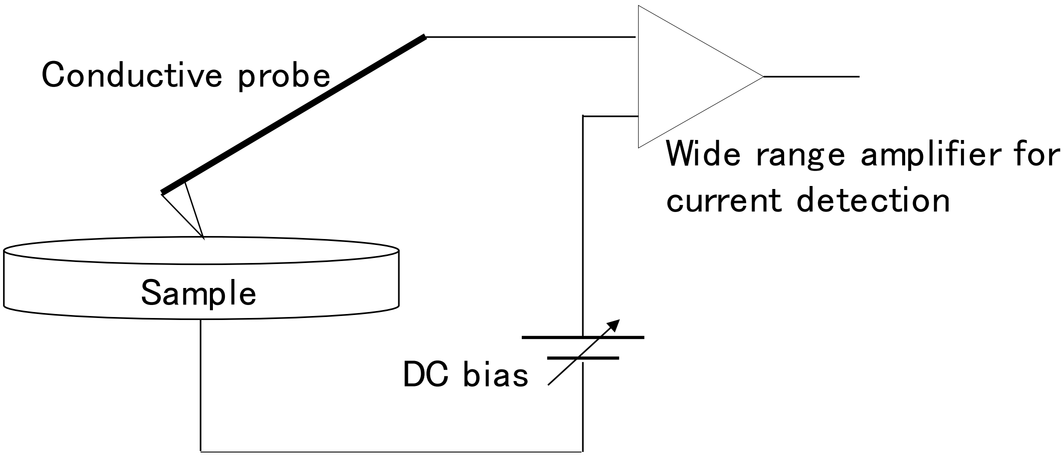

FIG. 5: Schematic of SPM used for tunneling current detection

The SPM probe used in this study is a silicon-nitride-based cantilever with a platinum–iridium-coated tip (PeakForce TUNA, Bruker Japan K.K., spring constant = 0.4 N/m). Table 2 shows the measurement conditions used for all samples.

TABLE 2
CONDITIONS FOR SPM MEASUREMENT

Measured area	1 × 1 μm^2
Scan rate	0.18–0.20 Hz
Amplitude setpoint	250 mV
Drive amplitude	750–825 mV
DC bias	−1.5 V

Figure 6 shows three-dimensional images of SWCNTs and SWCNT bundles prepared by dispersing SWCNTs in acetone on a Si substrate without using a dispersant, followed by heating the substrate at 150°C to dry and vaporize the acetone. The figure also shows images of the current distribution at the same locations. Figures 6(a) and 6(b) are images of HC-SWCNTs and Figs. 6(c) and 6(d) are images of SWCNTs with crystal defects. In the images of the current distribution, the dark brown color represents the areas in which electric current is detected. The areas are arranged almost in the shape of CNTs. These images show that in SWCNTs with crystal defects, the areas in which electric current is detected are more discontinuous than those in HC-SWCNTs and that electric current does not flow homogeneously in some areas. Also, contact resistance occurs at the contact points among CNTs or CNT bundles. In particular, electric current is not detected because of the high contact resistance at many of the contact points among the SWCNTs with crystal defects. Figure 7 shows the current–voltage (*IV*) characteristics at selected contact points in each sample. The measurement points are indicated by arrows in Fig. 6 (points A–F). The graph shows that the contact resistance in SWCNTs with crystal defects is relatively high compared with that in HC-SWCNTs. Because the internal resistance of CNTs is inhomogeneous, it is assumed that the areas of CNTs with high internal resistance come into contact with each other with high probability, making it difficult for electric current to flow. The contact resistance of the samples is depended on the crystallinity of CNTs can be determined from the *IV* characteristics of these samples. The above results indicate that the electric current flowing through SWCNTs depends on their crystallinity.

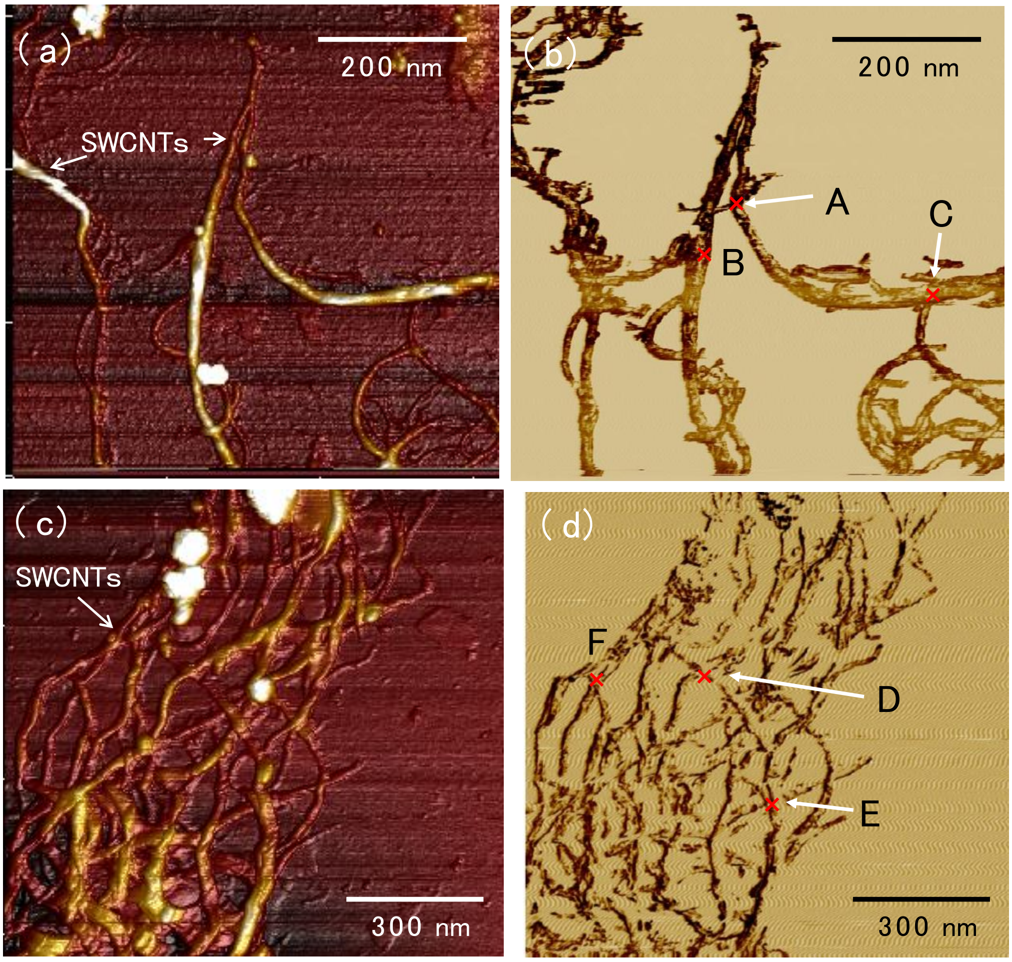

FIG. 6: SPM images.
(a), (c) Three-dimensional images and (b), (d) distribution of electric current induced by applied voltage. (a), (b) HC-SWCNTs dispersed on a Ta substrate and (c), (d) SWCNTs with crystal defects.

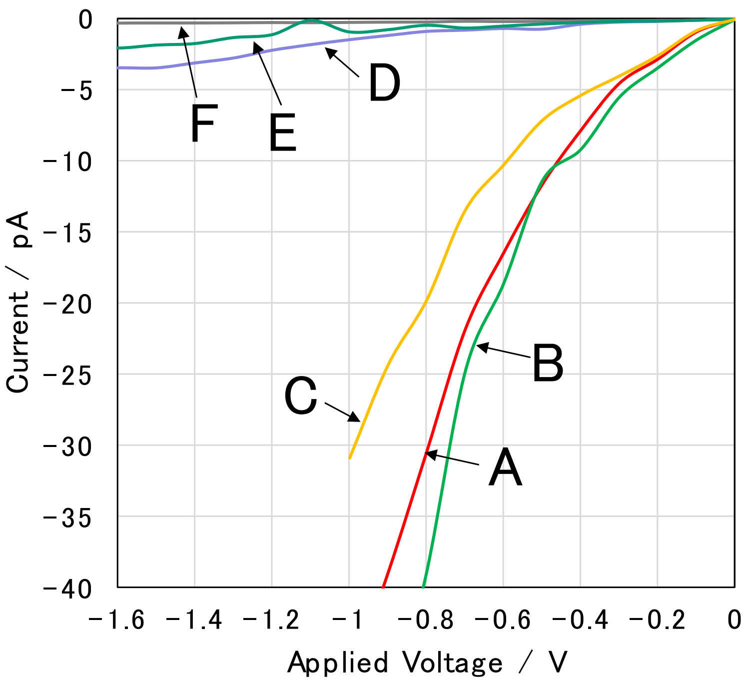

FIG. 7: IV characteristics at points A–F indicated by arrows in Figs. 6(b) and 6(d).

From Figs. 4, 6, and 7, we found that the Hall mobility can be greatly improved by controlling the density of added SWCNTs (weight density) and their crystallinity. The reason for this is that the Hall mobility reflects the increase or decrease in the number of contact points among SWCNTs as a result of controlling the density of added SWCNTs, as well as the changes in the contact resistance among the SWCNTs and their internal resistance resulting from the control of crystallinity. It is assumed that the Hall mobility of 1,000 cm^2/Vs can be achieved because the contact resistance among CNTs is small in HC-SWCNTs and therefore, the electric charge passes through multiple contact points (indicated by blue circles in Fig. 8) forming the shortest path in accordance with the density and arrangement of CNTs [Figs. 8(a) and 8(b)]. On the other hand, a path for the flow of electric charge is formed less easily in SWCNTs with crystal defects because of the higher internal resistance and contact resistance of the CNTs. The electric charge takes a less direct path as shown in Fig. 8(c), resulting in the low Hall mobility.

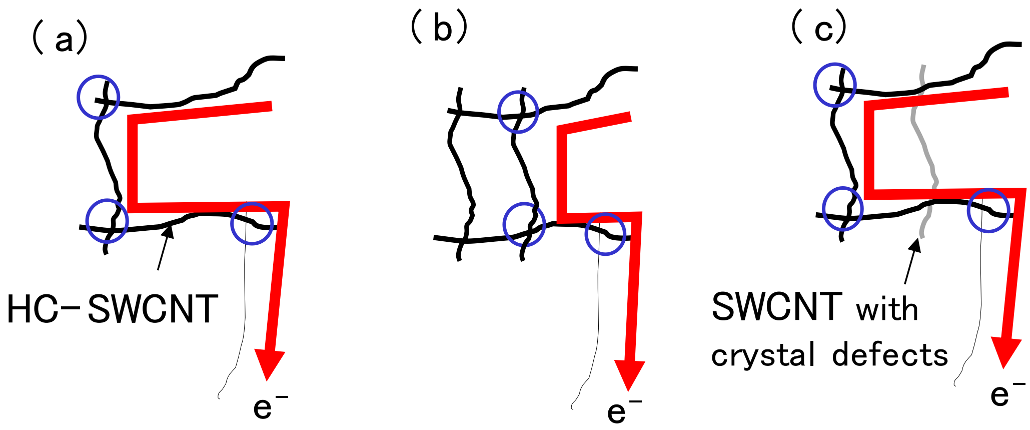

FIG. 8: Paths of electrons flowing through SWCNTs

IV. CONCLUSION

In this study, we fabricated SWCNT-containing thin films by a wet-coating process and evaluated the dependence of the Hall mobility on the weight density of added SWCNTs per unit area and the crystallinity of SWCNTs. Because CNTs, including SWCNTs, have semiconductive or metallic conductive properties, studies have been carried out with the aim of fabricating semiconductive thin films containing semiconductive SWCNTs and taking advantage of their properties. However, the research and development of practical applications of SWCNT-containing thin films have been limited because the handling and control of SWCNTs are difficult owing to their fibrous form, and the homogeneous dispersion of SWCNTs by a wet-coating process is also difficult. Our research team has developed a technology to disperse SWCNTs without impairing their crystallinity and succeeded in fabricating thin films from a dispersion liquid of SWCNTs obtained by this technology. We also evaluated the Hall mobility of these thin films and found that a high Hall mobility of 1,000 cm^2/Vs can be achieved by controlling the crystallinity.

The analysis of the conductive characteristics of SWCNTs using an SPM for tunneling current detection revealed that the resistance characteristics of SWCNTs depend on their crystallinity. Although it has been theoretically predicted that the conductive characteristics of CNTs depend on their crystallinity[47], this was the first time ever that the crystallinity dependence of conductive characteristics was demonstrated by an SPM-based analysis. The control of the Hall mobility of thin films was realized by using highly crystalline CNTs, including HC-SWCNTs, and controlling the weight density of the CNTs contained in the thin films. The results of this study showed the possibility of using CNT-containing semiconductive films formed on a substrate of arbitrary shape as ubiquitous devices. It is expected that the electron mobility of thin films will be further increased by synthesizing SWCNTs with zero defects and improving the composition of SWCNT thin films as well as that of the ITO matrix. On the basis of the results of this study, we will pursue our research to establish a technology for packaging electronic circuits that take full advantage of the electronic properties of HC-SWCNTs by a wet-coating process, and thus, to develop environmentally friendly semiconductor devices with high packaging density. Our goal is to realize thin films with low energy losses exhibiting a Hall mobility that is near the theoretical value for CNTs.

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REFERENCES

[1] Zhang, K.; Li, G.-H.; Feng, L.-M.; Wang,N.; Guo, J.; Sun, K.; Yu, K.-X.; Zeng, J.-B.; Li, T.; Guo, Z.; Wang, M. Ultralow percolation threshold and enhanced electromagnetic interference shielding in poly(L-lactide)/multi-walled carbon nanotube nanocomposites with electrically conductive segregated networks. *J. Mater. Chem.***2017**, *C 5(36)*, 9359-9369.

[2] Kim,K. S.; Zhao,Y.; Jang,H.; Lee,S. Y.; Kim,J. M.; Kim,K. S.;Ahn,J.-H.; Kim,P.; Choi,J.-Y.; Hong, B. H. Large-scale pattern growth of graphene films for stretchable transparent electrodes. *Nature***2009**,*457*, 706–710.

[3] Kim,D.-H.;Ahn,J.-H.; Choi,W. M.; Kim,H.-S.; Kim,T.-H.; Song,J.; Huang,Y. Y.; Liu,Z.; Lu,C.; Rogers, J. A. Stretchable and foldable silicon integrated circuits. *Science***2008**, *320*, 507–511.

[4] Sekitani,T.;Noguchi,Y.; Hata,K.; Fukushima,T.; Aida,T.; Someya,T. A rubberlike stretchable active matrix using elastic conductors.*Science***2008**, *321*, 1468–1472.

[5] Stutzman,N.; Friend,R. H.; Sirringhaus,H.Self-aligned, vertical-channel, polymer field-effect transistors. *Science***2003**, *299*, 1881-4.

[6] Dimitrakopoulos,C. D.;Purushothaman,S.;Kymissis,J.;Callegari,A.; Shaw,J. M.Low-Voltage Organic Transistors on Plastic Comprising High-Dielectric Constant Gate Insulators. *Science***1999**, *283*, 822.

[7] Dimitrakopoulos,C. D.;Malefant,P. R. L.Organic Thin Film Transistors for Large Area Electronics. *Adv. Mater.***2002**, *14*, 99-117.

[8] Nomura,K.;Ohta,H.; Takagi,A.;Kamiya,T.; Hirano,M.; Hosono,H.Room-temperature fabrication of transparent flexible thin-film transistors using amorphous oxide semiconductors. *Nature***2004**, *432*, 488-492.

[9] Nomura,K.;Ohta,H.; Ueda,K.;Kamiya,T.; Hirano,M.; Hosono,H.Thin-Film Transistor Fabricated in Single-Crystalline Transparent Oxide Semiconductor.*Science***2003**, *300*, 1269-1272.

[10] Geim,A. K.;Novoselov,K. S. The rise of graphene. *Nature Mater.***2007**, *6*, 183–191.

[11] Lee,C.; Wei,X.;Kysar,J. W.; Hone,J. Measurement of the elastic properties and intrinsic strength of monolayer graphene. *Science***2008**, *321*, 385–388.

[12] Cao,Q.; Rogers,J. A.Ultrathin Films of Single-Walled Carbon Nanotubes for Electronics and Sensors: A Review of Fundamental and Applied Aspects.*Adv. Mater.***2009**, *21(1)*, 29-53.

[13] Bauhofer,W.; Kovacs, J. Z. A review and analysis of electrical percolation in carbon nanotube polymer composites.*Comp. Sci.and Tech.***2009**, *69(10)*, 1486-1498.

[14] White,K. L.; Shuai,M.; Zhang,X.; Sue,H.-J.; Nishimura,R.Electrical conductivity of well-exfoliated single-walled carbon nanotubes.*CARBON***2011**, *49(15)*, 5124-5131.

[15] Shimoi,N.; Adriana,L.E.; Tanaka,Y.;Tohji, K. Properties of a field emission lighting plane employing highly crystalline single-walled carbon nanotubes fabricated by simple processes.*CARBON***2013**, *65*, 228-23.

[16] Garrido,S. B.; Shimoi,N.; Abe,D.; Hojo, T.; Tanaka,Y.; Tohji,K. Planar light source using a phosphor screen with single-walled carbon nanotubes as field emitters. *Rev. Sci. Inst.***2014**, *85*, 104704.

[17] Martel,R.; Schmidt,T.; Shea,H. R.; Hertel,T.;Avouris, P.Single- and multi-wall carbon nanotube field-effect transistors. *Appl. Phys.Lett.***1998**, *73*, 2447.

[18] Tans,S. J.;Verschueren,A. R. M.; Dekker, C. Room-temperature transistor based on a single carbon nanotube.*Nature***1998**, *393*, 49-52.

[19] Duan,X. F.;Niu,C. M.;Sahi,V.; Chen,J.;Parce,J. W.; Empedocles,S.; Goldman,J. L.High-performance thin-film transistors using semiconductor nanowires and nanoribbons. *Nature***2005**, *425(6955)*, 274-278.

[20] Elias,D. C.; Nair,R. R.; Mohiuddin,T. M. G.; Morozov,S. V.; Blake,P.; Halsall,M. P.; Ferrari,A. C.;Boukhvalov,D. W.;Katsnelson,M. I.;Geim,A. K.;Novoselov,K. S. Control of graphene's properties by reversible hydrogenation: evidence for graphene. *Science***2009**, 323, 610–613.

[21] Javey,A.; Guo,J.; Wang,Q.; Lundstrom,M.; Dai,H. Ballistic carbon nanotube field-effect transistors.*Nature***2003**, *424*, 654.

[22] Durkop,T.; Getty,S. A.;Cobas,E.; Fuhrer, M.S. Extraordinary Mobility in Semiconducting Carbon Nanotubes.*Nano Lett.***2004**, *4*, 35-39.

[23] Bradley,K.; Gabriel,J.-C. P.; Star,A.;Gru¨ner, G. Short-channel effects in contact-passivated nanotube chemical sensors.*Appl. Phys. Lett.***2003**, *83*, 3821.

[24] Bradley,K.; Gabriel,J.-C. P.;Gru¨ner, G. Flexible Nanotube Electronics.*Nano Lett.***2003**, *3*, 1353-1355.

[25] Gabriel,J.-C. P. Large Scale Production of Carbon Nanotube Transistors: A Generic Platform for Chemical Sensors. *MRS Proc.***2003**, *776*, Q12.7.

[26] Snow,E. S.; Novak,J. P.; Campbell,P. M.; Park, D. Random networks of carbon nanotubes as an electronic material.*Appl. Phys. Lett.***2003**, *82*, 2145.

[27] Szeluga,U.;Kumanek,B.;Trzebicka, B.Synergy in hybrid polymer/nanocarbon composites. A review.*Compos. A***2015**, *73*, 204-231.

[28] Ram,R.; Rahaman,M.; Khastgir,D. Electrical properties of polyvinylidene fluoride (PVDF)/multi-walled carbon nanotube (MWCNT) semi-transparent composites: Modelling of DC conductivity. *Compos. A*,**2015**, *69*, 30-39.

[29] Ebbesen,T.W.; Lezec,H. J.; Hiura,H.; Bennett,J. W.; Ghaemi,H. F.; Thio, T. Electrical conductivity of individual carbon nanotubes. *Nature* **1996**, *382(6586)*, 54-56.

[30] Bunch, J. S. et al. Impermeable atomic membranes from graphene sheets. *Nano Lett.***2008**, *8*, 2458–2462.

[31] Wang,X.; Li,X.; Zhang,L.; Yoon,Y.; Weber,P. K.; Wang,H.; Guo,J.; Dai1,H.N-doping of graphene through electrothermal reactions with ammonia. *Science***2009**, *324*, 768–771.

[32] Azoubel,S.; Shemesh,S.; Magdassi,S.Flexible electroluminescent device with inkjet-printed carbon nanotube electrodes.*Nanotechnology***2012**, *23(34)*, 344003.

[33] Saito,Y.; Uemura,S. Field emission from carbon nanotubes and its application to electron sources.*CARBON*, **2000**, *38(2)*, 169-182.

[34] Cao,Q.; Kim,H.-S.; Pimparkar,N.; Kulkarni,J. P.; Wang,C. J.; Shim,M.; Roy,K.; Alam,M. A.; Rogers, J. A.Medium-scale carbon nanotube thin-film integrated circuits on flexible plastic substrates. *NATURE***2008**, *454(7203)*, 495-U4.

[35] Balberg, I. TUNNELING AND NONUNIVERSAL CONDUCTIVITY IN COMPOSITE-MATERIALS.*Phys. Rev. Lett.***1987**, *59(12)*, 1305-1308.

[36] Tohji,K.; Goto,T.; Takahashi,H.; Shinoda,Y.; Shimizu,N.; Jeyadevan,B.; Matsuoka,I. ; Saito,Y.; Kasuya,A.; Ohsuna,T.; Hiraga,K.; Nishina, Y. Purifying single-walled nanotubes. *NATURE***1996**, *383(6602)*, 679.

[37] Iwata,S.; Sato,Y.; Nakai,K.; Ogura,S.; Okano,T.; Namura,M.;Kasuya,A.; Tohji,K.; Fukutani,K. Novel method to evaluate the carbon network of single-walled carbon nanotubes by hydrogen physisorption.*J. Phys. Chem. C Lett.***2007**, *111*, 14937-14941.

[38] Semenoff,G. W. Condensed-matter simulation of a three-dimensional anomaly. *Phys. Rev. Lett.***1984**, *53*, 2449–2452.

[39] Zheng,Y.; T. Ando, T. Hall conductivity of a two-dimensional graphite system. *Phys. Rev. B* **2002**, *65*, 245420.

[40] Tan,H.-X.; Xu, X.-C.Conductive properties and mechanism of various polymers doped with carbon nanotube/polyaniline hybrid nanoparticles. *Comp. Sci. and Tech.***2016**, *128*, 155-160 .

[41] Haldane, F. D. M. Model for a quantum hall effect without Landau levels: condensed-matter realization of the "parity anomaly". *Phys. Rev. Lett.***1988**, *61*, 2015–2018.

[42] Zhang,Y. B.; Tan,Y. W.; Stormer,H. L.; Kim, P.Experimental observation of the quantum Hall effect and Berry's phase in graphene. *NATURE***2005**, *438(7065)*, 201-204.

[43] Phang,I.-Y.; Liu,T.; Zhang,W.-D.; Scho¨nherr,H.; Vancso, G. J. Probing buried carbon nanotubes within polymer–nanotube composite matrices by atomic force microscopy.*European Polymer Journal***2007**, *43*, 4136–4142.

[44] Desbief,S.; Hergue,N.-E.; Douheret,O.; Surin,M.; Dubois,P.; Geerts,Y.; Lazzaronia,R.; Leclere, P. Nanoscale investigation of the electrical properties in semiconductor polymer–carbon nanotube hybrid materials.*Nanoscale***2012**, *4*, 2705.

[45] Yang,X.; Liu,R.; Lei,Y.; Li,P.; Wang,K.; Zheng,Z.; Wang, D. Dual Influence of Reduction Annealing on Diffused Hematite/FTO Junction for Enhanced Photoelectrochemical Water Oxidation. *ACS Appl. Mater. Interfaces***2016**, *8*, 16476−16485.

[46] Herrer,L.; Sebastian,V.; Martín,S.; González-Orive,A.; Pérez-Murano,F.; Low,P. J.; Serrano,J. L.; Santamaríaa,J.; Cea, P. High surface coverage of a self-assembled monolayer by in situ synthesis of palladiumanodeposits.*Nanoscale***2017**, *9*, 13281.

[47] Shimoi,N. Effect of increased crystallinity of single-walled carbon nanotubes used as field emitters on their electrical properties. *J. Appl. Phys.***2015**, *118*, 214304.