Ph.D. DISSERTATION

Electrical and Structural Properties of Inkjet-Printed Single-Walled Carbon Nanotube Thin Film, and Its Applications

잉크젯 프린팅 공정 기반 단일벽 탄소나노튜브 박막의 전기적, 구조적 특성 및 응용

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DEPARTMENT OF ELECTRICAL ENGINEERING
AND COMPUTER SCIENCE
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Abstract

Electrical and Structural Properties of Inkjet−Printed Single−Walled Carbon Nanotube Thin Film, and Its Applications

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Recently, flexible and stretchable features have been introduced for the use in various devices such as sensor, thin film transistor, and organic light−emitting diode. Advance developments in terms of materials, device physics, chemistry, and mechanics allow various devices to sustain their performance under deformation. But, many researches are still required to achieve stretchable electronic

devices having high performance. Among the element, it is expected that the materials have an important role and lead to high performance.

A carbon nanotube is one of the promising materials for the use in the stretchable electronics due to its excellent properties resulted from unusual structure of the carbon nanotube. In addition, tunable properties using functionalized group on the tube are advantages of the carbon nanotube. So, the use of carbon nanotube in stretchable electronics has been increased using the excellent properties. However, some technical issues such as low dispersion stability, scalability, and lower properties than individual carbon nanotube remain, which should be solved.

First, we used an inkjet printer to improve the low scalability. In contrast to spin coating or screen printing reported in previous paper, the inkjet printing system reduces loss of materials; this is advantage for the use of single-walled carbon nanotube that suffers from high cost. Instead of the organic solvent having toxicity, the single-walled carbon nanotube was dispersed in aqueous solution. The low dispersion stability of the single-walled carbon nanotube in the aqueous solution was solved using surfactant. The

synthesized ink was printed on stretchable substrate. Well−shaped film was obtained by controlling substrate temperature, UV ozone treatment. To reduce the surfactant used for dispersion stability, two post treatments (water rinsing and nitric acid treatment) were performed. Significant results of both treatments were confirmed from conductivity and structural properties.

The inkjet−printed single−walled carbon nanotube thin films exhibited excellent mechanical properties under deformation. The thin films did not lose conductivity in even high tensile strain (100%), and the conductivity was maintained in cyclic stretching test although little variation of resistance was shown. The specific phenomenon was confirmed from microstructure of the thin film, which was crack bridging of carbon nanotube. The property was demonstrated using a integration with light−emitting diode.

Response of the single−walled carbon nanotube thin film on the external strain could be controlled by structural properties of the thin film without loss of durability. Inkjet−printed pre−pattern caused cracks on the thin film, which improved the response on the external strain. When the conditions of the pre−pattern were optimized, the thin film had high sensitivity, durability, linearity. The printed thin films were demonstrated by detecting human motions. Strain sensor system consists of stretchable electrode and strain sensor were fabricated using tunable response of the inkjet−printed single−walled carbon nanotube thin film on the tensile strain.

주요어 : Inkjet−printing, Single−walled carbon nanotube, stretchable, strain sensor

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Chapter 1

Introduction

1.1 Motivation

Stretchable electronics is one of the hottest research areas in electronic applications, and it is evaluated as the promising next-generation electronics. Many researchers and groups tried to improve the stretchable electronics in term of material, device physics, chemistry, etc. Among the areas, the material affects the direction of the development significantly. A drastic improvement in the stretchable electronics is mainly achieved by continuous development in the carbon material such as carbon nanotube and graphene. And, it has still a lot of potential to improve the electronics, even to unpredictable direction; this potential is originated from unusual properties of the carbon material. It is interesting thing that the researches for the stretchable electronics using the carbon material showing unusual properties have been widely investigated in recently. To meet the recent research flow and respond the drastic development resulted from the carbon material, we should know the fundamental theory of the carbon material and recent approaches, and try to use the contents for solving some technical issues. In this chapter, it is introduced that the properties, application and ink fabrication method of the carbon nanotube in this chapter. The information of the carbon nanotube reported by other research group provides advantages of the processes and disadvantages reducing the properties of carbon nanotube. Based on the contents, we choose a synthesis method for well−dispersed carbon nanotube in aqueous solution, a fabrication method for a formation of carbon nanotube thin film, post treatments for improving the carbon nanotube thin film, and applications for the carbon nanotube thin film in next chapter.

1.2 Carbon nanotube

There are intense interests for carbon nanotubes in electronic applications due to their specific properties, not shown in other materials, since it was invented in 1991. [1] The structure of the carbon nanotube is a well–rolled graphene plate, and the size of the tube is determined by conditions in fabrication process such as catalyst or deposition technique. [2],[3] It is noted that graphene has excellent electrical properties owing to sp^2 bonding of carbon atom. The carbon nanotube, rolled graphene plate, has not only excellent electrical properties but also specific properties not observed in other carbon nanotube materials. [4]–[6] The specific properties resulted from unusual molecular structure could be used for various applications such as supercapacitor [7],[8], electrode application [9],[10], active materials in thin film transistor [11],[12], and various sensors. [13]–[15] To obtain good application, we should know the background theory and the properties of carbon nanotube exactly. And, we should take a fabrication method to improve the advantage of carbon nanotube and to reduce the disadvantage of the materials.

1.3 Properties of carbon nanotube

1.3.1 Structure of carbon nanotube

Carbon is 6th in the periodic table of the elements; the extra electrons in the subshell are four that are weakly bound electrons in the $2s^2 2p^2$ valence orbital except two strongly bound electrons in the $1s^2$ orbital. The electron occupations in the orbital are mixed and changed to improve the binding energy of the carbon atom and other atom because the energy gap between $2p$ energy level and $2s$ energy level is lower than the binding energy of the chemical bonds. This is called as sp^n hybridization; the name of the hybridization is determined by the number of $2p$ electron. In case of graphite, one carbon atom has covalent sp^2 bonding, mixed by one $2s$ electron and two $2p$ electrons, with neighboring three carbon atom to planar structure and the remained electrons in out-of-plane with weak bonding. [16],[17] The specific structure with one carbon atom and three carbon atoms bonded around the carbon atom has periodic lattice; the structure called by a honeycomb structure is base structure of graphene (one-atom-layer thick of graphite). [18] The structure of carbon nanotube is the wrapped graphene. The wrapping method of the graphene is determined by a pair of indices (n.m); the indices mean unit vector of two directions in honeycomb structure of graphene. [19],[20] There are some types of the carbon nanotube with different twisted structure. Each carbon nanotube is distinguished by some relationship of the indices formed by different twisted angle. When a relationship of unit vector to the direction of carbon nanotube presents m=0, it called zigzag nanotube. When the relationship has n=m, it called armchair nanotube. In other cases, the carbon nanotube is called by chiral, the angle with a vector for m=0 is called by chiral vector. To understand easily, zigzag nanotube has 0° of the chiral vector and armchair has 30°. [21]

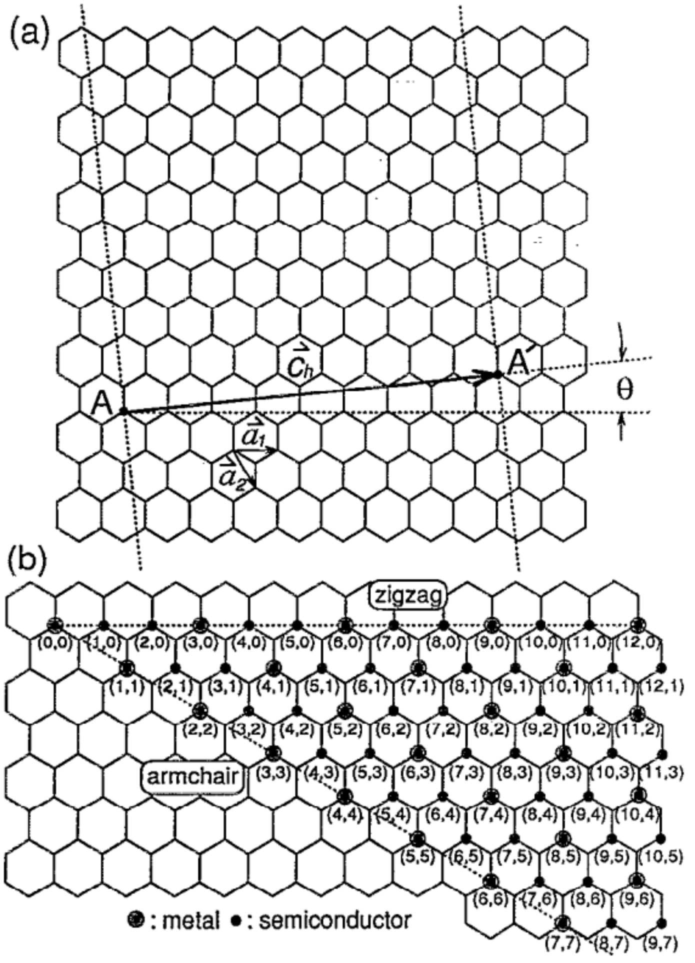


Fig. 1.1 (a) Carbon nanotube has tubular structure which are made by connecting A and A' in a graphene sheet. The structure of carbon nanotube and the twisted angle are determined by lattice vector $\mathbf{c}_h$ and θ, respectively. $\mathbf{a}_1$ and $\mathbf{a}_2$ denote the unit vector of the graphene sheet.

(b) Possible lattice vectors that consists of a pair of indices (n,m).

The circled dots and dots mean metallic and semiconducitng behavior for each point, respectively. A vector having indices (n,0; n is integer) is called by chiral vector, and some structure of carbon nanotube is determined by an angle between the chiral vector and lattice vector [25]

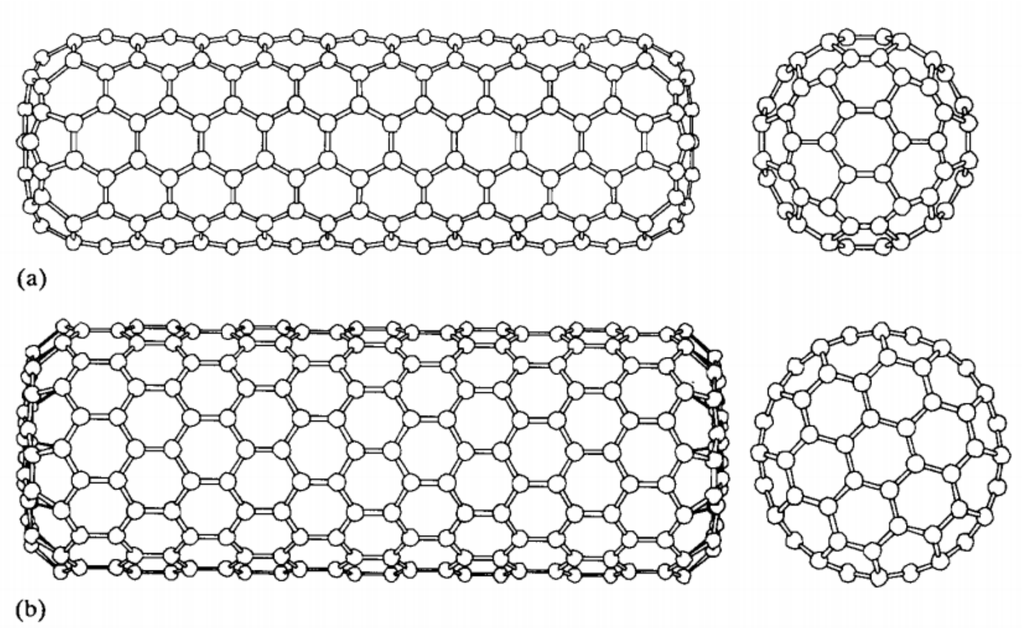


Fig. 1.2 Top and side view of two types of carbon nanotube (a) armchair structure, and (b) zigzag structure [26]

1.3.2 Electrical properties of carbon nanotube

Carbon nanotubes have been studied for specific electrical properties compared to the other carbon−related materials such as graphene having small band gap properties. [22],[23] In addition, a complex relationship of individual carbon nanotube should be considered to comprehend electrical properties of carbon nanotube thin film due to conduction mechanism between carbon nanotubes. [24] The individual carbon nanotube has two types of electrical properties determined by a chiral vector of the individual carbon nanotube, and the carbon nanotubes having two different properties are coexist in the thin film [25],[26]; it is hard work to consider the whole relationship. [27] The defect or other doped materials on the tube can affect electrical properties of the carbon nanotube significantly. [28],[29] In this chapter, we concentrate the fundamental theory and investigation for the electrical properties of carbon nanotube to confirm the feasibility of carbon nanotube in electronic application rather than to analyze the carbon nanotube statistically.

Carbon nanotubes have tubular structures with asymmetric ratio of width and diameter; the unusual electrical properties of carbon nanotube are strongly related with the structure of the carbon nanotube. [30] It is noted that a single-walled carbon nanotube has cylindrical structure by rolling a graphene sheet. The electrical properties of the single-walled carbon nanotube are sensitive to their structural properties and easily tunable using geometrical or chemical doping that cause the change of electrical transport on the surface of tube controls of carbon nanotube. [31],[32] In addition, the size of energy band gap of carbon nanotube is determined by the diameter of carbon nanotube. If the graphene sheet is not suppressed to external force and distorted, the diameter of carbon nanotube depend on the helicity of the tube. The helicity is specified by a pair of integers (n, m). The integers means a perpendicular vector to the direction of length, which is determined by the pair of atoms on a graphene sheet when the sheet forms the tube and the pair of atoms is connected. Based on the theoretical calculations, the general rules for electrical properties of the single-walled carbon nanotube are introduced using the vector in the graphene sheet as follows [33],[34]

$\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2$

The vector is called by a chiral vector; the chiral vector is one of the expressions to specify the carbon nanotube. There is one carbon nanotube having (n, m) tubes with n−m=3j where j is a nonzero integer; this is metallic carbon nanotube. In general, the case should be metals, but some case of carbon nanotube has a tiny band gap because of the curvature effect of the carbon nanotube although the j is nonzero integer. In other case, the carbon nanotubes have large gap semiconducting. [35] When the radius of the tube increases, the band gap of the semiconductor decreases with a 1/R dependence. [36] The crystallinity of carbon nanotube related with helicity could be tuned using atmosphere in the chamber during synthesis and other fabrication conditions. [37] The various characteristics of carbon nanotube determined by the structure provide a fascinating theme to study the electrical properties of the carbon nanotubes and a high possibility for the use in electronic application such flexible electronics.

To use the carbon nanotube in the electronic application, a recent advance of carbon nanotube−based device should be considered. After the carbon nanotube was invented by Ijima in 1991, the carbon nanotube−based devices have been widely investigated in various applications. Although the carbon nanotube−based devices fabricated in nanoscale showed fascinating results in the various applications due to the unusual properties of the individual carbon nanotube, [38],[39] it is hard to improve uniformity and scalability. [40] Recently, the interest of carbon nanotube for the use in the electronic application has been expanded to the larger scale devices. [41]-[44] However, most of them have problems in term of lower properties than the individual carbon nanotube. Compared with the individual carbon nanotube having excellent conductivity, thin film type has inferior electrical properties resulted from the carrier transport mechanism in tube-tube junction exhibited higher contact resistance than on-tube resistance. [45] When a carrier moves from one nanotube to another nanotube, a huge energetic loss take place in the interface region and a drastic reduction of conductivity occurs in the junction. There are some ideas to increase conductivity of the carbon nanotubes in the mixed system.

A doping is one of the compatible methods to improve electrical properties of carbon nanotube. Many functional groups could be attached on the carbon nanotube using the chemical treatments. [46]-[49],[146] The effect of the doped of grafted materials on the electrical properties of the carbon nanotube depends on the electron affinity of the groups. [50] In case of p-type doping materials, the group with high electron affinity pulls the electron in the carbon nanotube into the group. Acid materials are representative materials for p-type doping of the carbon nanotube to improve electrical properties. The doping effect on the electrical properties of carbon nanotube thin film has been studied with various analyses in previous reports. This is simple method to tune the electrical properties, but the improvement using some acid materials has degradation in air because the molecules weakly absorbed to the carbon nanotube surface will be unstable by the moisture. [51] In this aspect, other method using metal nanoparticle has good environmental stability without degradation after exposure to heat, water, isopropyl alcohol, and acetone. [52] The metal nanoparticles are attached on the surface of carbon nanotube using chemical treatment such as acid treatment. [53],[54] When some chemical treatments are performed subsequently, the mechanical adhesion between metal nanoparticle and carbon nanotube is improved; this improve the contact resistance at tube-tube junction. Although metal particle-mixed conductive composite is also reported, it is not a solution to reduce contact resistance. [55] The two methods, crafted or functionalized carbon nanotube, provide high feasibility and possibility for use in the electronic devices because the properties could be tuned to meet the needs

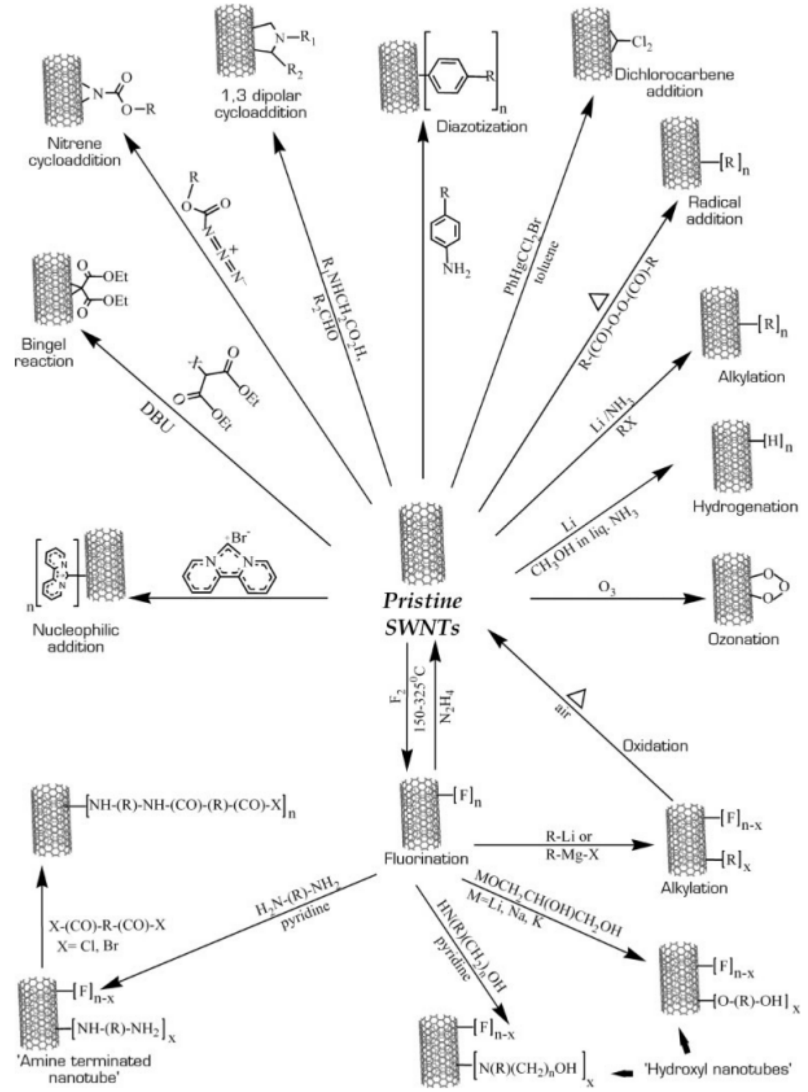


Fig. 1.3 Schematic map of various functionalized carbon nanotube [146] The covalent bonded functionalized groups on the surface affect the properties of the carbon nanotube.

1.3.3 Mechanical properties of carbon nanotube

It is well noted that mechanical properties of carbon nanotube is quite high owing to specific structure. In the structure of carbon nanotube, a covalent bonding formed by four carbon atom is well known as sp^2 hybridized carbon atoms tightly bonded with a bonding angle of 120 degree. In the honeycomb structure formed by periodic lattice of the covalent bond, a quite strength is required to distort the periodic lattice or to move bonded atom into the other lattice; this means the carbon nanotube has good resistance to the tensile stress and elastic deformation. [56],[57] To confirm the mechanical properties such as Young' s modulus and tensile stress of a carbon nanotube, many researches have been studied. [58]-[61]

The excellent mechanical properties resulted from its unusual structure could be used in various applications. An addictive improving a toughness of base materials in cement mixture is the best method using the mechanical properties of the carbon nanotube. [62],[63] The carbon nanotube in the cement, strength but brittle, prevent fracture of the ceramic material. When a crack takes place in a certain region, the crack propagates to the whole region by applied force. The carbon nanotube randomly mixed in the material reduces the velocity of crack propagation due to its excellent mechanical properties. It is very useful method for brittle materials and widely studied for various base materials. [64]

Unlike a single walled carbon nanotube with high Young' s modulus and tensile stress, a significant reduction of the mechanical properties occur in case of thin films and composites. [65],[66] The low mechanical properties resulted from the bonding between each carbon nanotube. In case of individual carbon nanotube, the periodic lattice of carbon atom in the honeycomb structure disturb distortion of the lattice; this improve the mechanical properties of the individual carbon nanotube. However, main force affecting the bonding between each carbon nanotube in the bundles or thin film is van der Waals force known for weak bonding force than covalent sp^2 bonding in the honeycomb structure. Only a weak tensile stress could apart each carbon nanotube and causes a crack in the film. Some papers reported layer-by-layer self-assembly method to improve the mechanical properties using electrostatic force between each layer. [67]-[69]

In addition, there are other structural efforts that have been used in stretchable electronics recenlty. A wrinkled structure is one of the solutions to improve resistance of deformation when external stress is subjected. [71],[72] The pre-strain applied to the substrate before deposition of carbon nanotube improve stretchability of the deposited thin film. The electrical properties of the thin film are maintained in high strain range compared to the results on bare substrate. Recently, the wrinkled structure is widely used in various applications such as supercapacitor [72] and photovoltaic cell. [73] The high dependency on the mechanical properties of the substrate to fabricate wrinkled structure is the drawback of this wrinkled structure.

The other solution is an intended fracture in the thin film of bundles of carbon nanotube. The electrical properties of thin film formed by carbon nanotube have a reduction when tensile stress is induced. The external force cause a crack, and reduced electrical properties. Conversely, the crack in the thin film of carbon nanotube does not propagate when maximum stress is same. Ii is so called by "programming" usually observed in stretchable electronics based on the carbon nanotube. [74]-[76] The phenomenon is originated from the excellent mechanical properties of individual carbon nanotube. The phenomenon has high potential to the stretchable electronics, but low electrical properties reduced from the initial stress should be solved

1.3.4 Other properties of carbon nanotube

Carbon nanotube is the most famous materials having versatility in many areas, which results from the unique structure of the carbon nanotube. In previous chapter, the electrical and mechanical properties of the carbon nanotube were introduced to inform the utility of the material. There are still excellent properties of carbon nanotube to use the material in various devices. The individual carbon nanotube has a large optical absorption band at 4.5 eV originated from π−plasmon of carbon nanotube and low optical absorption in other energy level relatively. [77] The optical absorption is determined by the diameter of carbon nanotube resulted from different catalysts in the synthesizing process. [78] The optical absorption of the carbon nanotube, although it has some variation and little optical absorption occur in low photon energy, raises the use of transparent conducting thin film. The transparent conducting thin films of the carbon nanotube have been widely reported in various applications such as electrode application for organic solar cell. [79]−[81] However, a graphene sheet synthesized in large area has been focused in the application of transparent conducting film in recently because of some technical issues and problems of carbon nanotube. [82],[83] To use the carbon nanotube thin film for transparent conducting film, some problems such as carrier transport in tube−tube junctions should be solved.

Thermal conductivity of the carbon nanotube is also advantage in the properties. The single and multi−walled and carbon nanotube have been studied for high thermal conductivity [84],[85]. It is originated from phonons on the carbon nanotube having long−range crystallinity in the structure. The structure of carbon nanotube provides the longitudinal thermal conductivity; this exceeds the in−plane thermal conductivity of graphite. [86] The high thermal conductivity of carbon nanotube resulted in the dissipating heat in various electronic applications has high potential for the use of carbon nanotube. [87]

1.4 Dispersions of carbon nanotube

Since the carbon nanotube was invented, various fabrication methods have been tested for uniform film or composite. In most case of fabrication method, dispersion stability of carbon nanotube in a certain solvent is critical and difficult issue for high uniform film or composite. And, it is difficult issue to disperse carbon nanotube in a certain solvent. In this chapter, fabrication methods of ink or composite for carbon nanotube−based devices will be introduced.

1.4.1 Fabrication ink for a solution process

An ink is fabricated by solvent, material powder and additive for controlling viscosity or dispersion stability or adhesion. The ink is usually used for printing or coating method which require low viscosity. It is well noted that carbon nanotube disperse in aqueous solution is very difficult thing without any changes in the structure of the carbon nanotube. [88],[89] The solvent for dispersing carbon nanotube prefers organic solvent with functionalized group [89] or non−hydrogen−bonding based on Lewis base [90] than aqueous solvent. Although many groups investigating carbon nanotube have used organic solvents for ink synthesis and dispersion stability, the organic solvent is harmful mostly. [91],[92] To avoid the hazard situation, it has been tried to fabricate carbon nanotube-based aqueous solution using some additive. A surfactant is the most famous addictive materials for improving the dispersion stability of the carbon nanotube in aqueous solution. [93] The surfactant was coated on the surface of the carbon nanotube; this provides steric repulsive force which prevents the carbon nanotube agglomerating. [94],[95] The agglomeration of carbon nanotube in the solution is originated from van der Waals force activated between the carbon nanotubes. The carbon nanotube-based solution with surfactant has a colloidal structure results from the steric repulsive force of the surfactant and has good dispersion stability. [96] Sodium dodecyl sulfate (SDS), Triton X-100 (TX-100) and sodium dodecylbenzene sulfonate (SDBS) are well-known materials for the dispersion stability of the carbon nanotube. But the maximum concentration of carbon nanotube in the surfactant-dissolved solution is low. [97] In addition, it raises another technical issue for elimination of the dissolved surfactant which could affect the properties of carbon nanotubes. [98]-[100]

A method of surface functionalization has advantage in term of the side effect of the surfactant. When the structure of carbon material having honeycomb structure with sp^2 bond and π electron were transformed by acid or polymer materials, the van der Waals force activated between carbon nanotubes become weaker. [101] The properties of carbon nanotube also changes slightly. In general, acid materials have been used for the surface functionalization. To improve the effect of the surface functionalization, the acid treatment is performed with thermal oxidation. When the carbon nanotube have a process consist of boiling in the acid solution and thermally oxidation, the carbon nanotubes has functional group on their surface such as carboxylic, hydroxyl and carbonyl. [102] But, the properties of carbon nanotube could be also changed by the defect formed during the oxidation process. [103] The above mentioned methods to improve the dispersion stability of carbon nanotube have disadvantages each other. Among them, the method compatible with the process have to be selected.

1.4.2 Fabrication carbon nanotube composites in polymer matrix

A carbon nanotube–polymer composite was reported in 1994, and the composite consists of multi–walled carbon nanotube and epoxy. [104] After the invent, the polymer composites with carbon nanotube have widely studied in many research groups to improve the uniformity of the carbon nanotube in the polymer. But it is difficult thing to achieve the uniform dispersion due to viscosity of polymer compared to the viscosity of water or alcoholic solvent. To obtain the well–dispersed carbon nanotube in the polymer, there are some methods. The basic concept is the dispersion of the carbon nanotube into a monomer, and then, polymerized using heat or curing agent. [105] If the carbon nanotube in the monomer suffer low performance from the debundle state caused by high viscosity of the polymer, the dispersion of the carbon nanotube into a liquid solution that contains dissolved or dispersed monomer. In that case, the liquid that contains the monomer and the carbon nanotube–dispersed liquid should be miscible. The liquid used for the dispersion should be evaporated before polymerization. Also, the liquid should not interfere with the polymerization of the monomer and the properties of composite. Polyvinylalcohol (PVA), polystryrene (PS), and poly(methyl methacrylate)(PMMA) are well known materials for the polymer–based composite. [106]–[108]

Recently, some polymers showing stretchable properties such as poly(dimethlysiloxane) (PDMS) have been studied for the matrix material of the carbon nanotube−based composite to apply their mechanical properties. [109]−[110]

1.5 Applications of carbon nanotube

The carbon nanotube is one of the most useful materials with versatile and excellent properties due to its structure. Since the carbon nanotube was invented in 1991, various applications have been reported using the properties. The range of the application varies from electrode application to semiconducting materials. In this chapter, the application will be introduced.

1.5.1 Stretchable electronics

Stretchable electronics is not only the meaning of some electronic devices, but also a system with platform, electronic device and electrode applications. [111]−[113] The stretchable electronics is regarded as next−generation electronics, the system do not lose its performance under harsh conditions compared to the flexible electronics. To overcome the harsh conditions, systematic approaches of all components in the stretchable electronics are required. The carbon nanotube is one of the best candidates for components in the stretchable electronics, except platform based on elastic polymers. In this chapter, the stretchable components using carbon nanotube are introduced.

The use of the carbon nanotube in the stretchable electronics has become hottest topic since T. Someya's group reported stretchable electrode application of the carbon nanotube in 2008. [114] Although a single walled carbon nanotube has high tensile strength and maintain the tubular structure in tensile strain up to 16% resulted from the unusual structure of carbon nanotube and high binding energy of sp^2 covalent bond, bundle structure has low mechanical properties because bonding energy between each carbon nanotube in the bundle is weak as van der Waals force as mentioned in previous chapter. To improve the stretchablility of single walled carbon nanotube in the bundle, they used PDMS and ionic liquid as polymer matrix material and additive for dispersion stability of carbon nanotube in the polymer matrix, respectively. The stretchable composite has good stretchability of 118%. The Stretchable composite maintained electrical properties in high strain range; the compliant properties of the composite realize the stretchable active matrix array for thin film transistor and organic lighting-emitting diode. [115] In addition, viscous paste with carbon nanotube for screen printing having advantage of scalability could be fabricated by slight changes during synthesis processes.

However, conductivity of the stretchable composite is still low to meet the requirement of electronics devices. In 2012, silver nanoparticles were attached on the carbon nanotube to improve the conductivity of the carbon nanotube. [54] In addition, silver nanoflakes were also mixed for conducting composite; the silver nanoflakes take a role of bridge between each carbon nanotube having conduction mechanism of hopping. When silver nanoflakes contacted silver nanoparticles on the carbon nanotube, a current easily moves to other nanotube. Modified contents of silver flake in the conducting nanocomposite improve conductivity of the composite under deformable conditions because a possibility of contact between silver nanoflake and nanoparticle increase.

Various sensor applications are also studied in the stretchable electronics. Since the sensor can measure a tiny change, the harsh conditions such as tensile stress that cause a change are hard to obtain exact results in the stretchable electronics. So, an investigation on sensor for the stretchable or flexible electronics is challengeable, and various stimuli could be targeted for the stretchable or flexible sensor. [116]–[118] Among the stretchable sensor measuring stimulus, pressure sensors have been widely studied for an electronic skin substituting human skin for replacing the role. The pressure sensor could measure applied pressure on the sensor, and the measurable pressure range of the sensor varies by fabrication method, materials and sensor structure. A most famous pressure sensor was reported by Z. Bao's group in 2012. [75] They used spray-coated single walled carbon nanotube thin film on PDMS substrate; the thin film has specific phenomenon in microstructure during stretching-releasing cyclic test. Because of the specific phenomenon, the single walled carbon nanotube thin films do not lose their sensing properties when tensile stress is subjected. A transparent pressure sensor with sandwiched structure of the single walled carbon nanotube thin films has capacitive type for sensing the applied pressure; it can measure the spatial distribution of applied pressure.

Strain sensors are most useful sensor in the stretchable electronics for sensing applied strain to the platform in the electronics. Since strain sensor was invented for sensing strain in the structure, bridge, and ship, the sensor has been widely used in various areas such as structure, sports, rehabilitation and analysis of materials. [119]-[121] Recently, strain sensors for the use in human−motion detector get become the most intensive research area to meet the need for increasing interest. While a strain sensor used for detecting crack or fatigue in building or structure should have high sensitivity to sensing a tiny change, the strain sensor for human−motion detection requires improved stretchability, stability during dynamic action and durability. The former is mostly focused on semiconducting−based strain sensor having high sensitivity to the applied strain, and the latter is focused on conducting composite−based strain sensor having high stretchability. Normally, skin of human or rat maintains its elastic properties in the strain range of 30~50%. [122],[123] When a higher tensile strain than the strain range is subjected to the skin, the skin has fracture or loses its intrinsic properties of elastic. As consider the above mentioned conditions, strain sensor should have wide strain range; the semiconducting−based strain sensor does not meet the conditions of strain range due to low stretchability.

To solve this problem and obtain strain sensor with wide strain range, various types of strain sensor have been investigated by using different materials. [124]−[126] The sensitivity of the strain sensor is determined by fabrication methods, materials, structures and other issues. Many groups have modified their studies for improving properties of the strain sensor. However, it is still hard to clear trade−off between sensitivity and strain range of strain sensor.

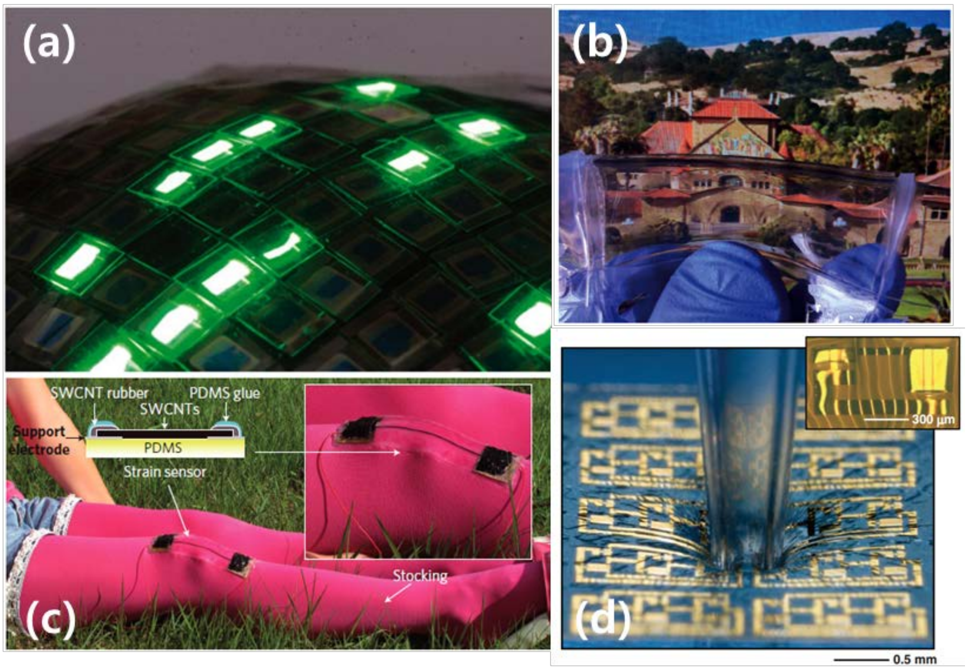


Fig. 1.4 Various stretchable electronic applications (a) Stretchable electrode integrated with organic light emitting diode, (b) Pressure sensor, (c) Strain sensor, and (d) Silicon circuit [74],[75],[111],[115]

1.5.2 Thin film transistor

As mentioned in previous chapter, the radius and chiral vector of single walled carbon nanotube affect the band gap of the carbon nanotube. Although there are some changes by types of energy source during fabrication method, the ratio of metallic and semiconducting single walled carbon nanotube in the manufactured carbon nanotube is 1:2. [33],[127] Commercial powder of carbon nanotube fabricated by the CVD method has also the ratio of mixture; this means that a separation process of mixed carbon nanotube powder is required to use each carbon nanotube. Especially, a few metallic carbon nanotube in the bundles of semiconducting carbon nanotube causes low switching properties of thin film transistor having active material of semiconducting carbon nanotube. Rather than electrode applications using the conductivity of the carbon nanotube, semiconducting properties of carbon nanotube are sensitive to the concentration of metallic carbon nanotube. To reduce the concentration of metallic carbon nanotube in the thin film of semiconducting carbon nanotube, there are many papers investigating separation process of the mixed carbon nanotube. [128]-[130] Before 2000, separation process using filtration or transfer technique was reported to fabricate electronic devices such as logic circuit. But, the previous technique has many disadvantages to enlarge a scale of the electronic device.

Two technique reported in the recent lead to a great improvement of thin film transistor based on semiconducting carbon nanotube. One is surface treatment, and the other is density gradient ultracentrifugation (DGU). [131] Z.Bao' s group had reported the surface treatment on substrate to improve the selectivity of the substrate to the carbon nanotube. They reported surface treated substrate using two different organic chain groups such as phenyl and amine group preferred metallic and semiconducting carbon nanotube, respectively. The results were confirmed by Raman spectroscopy, and semiconducting-enriched thin film showed switching properties. 3-Aminopropyltriethoxysilane(APTES) materials used for the attachment of the amine organic group to the substrate is critical material and many paper studied after the first report for surface treatment has used the material of surface treatment. In addition, other material for surface treatment on substrate to improve preference on semiconducting carbon nanotube is also reported. [132]

Above mentioned in previous chapter, a diameter of carbon nanotube is related with the band gap energy of carbon nanotube. A density gradient ultracentrifugation method is based on the difference of diameter of carbon nanotube, When two noncovalent surfactant are applied to the solution of carbon nanotube powder, the surfactants interact with a layer of carbon nanotube. Two types of carbon nanotube are covered with the surfactant, and the surfactant−covered carbon nanotube has different buoyant densities due to different diameters of each carbon nanotube. The buoyant densities of carbon nanotube is determined by concentration of two surfactant attached on carbon nanotube. By the different buoyant of the surfactant−covered carbon nanotube, it has gradient separation during centrifugation in extremely high speed. To improve the concentration of the each carbon nanotube, some conditions such as the ratio of two surfactants and the number of centrifugation are adjusted. After ultracentrifugation, each layer in the solution is separated with different optical absorption spectra. The separation technique makes a great improvement on the study for thin film transistor due to mass production of semiconducting−enriched aqueous solution.

Before 2010, some researches for thin film transistor based on semiconducting−enriched ink have been focused to obtain fundamental properties of semiconducting single walled carbon nanotube. [12],[133] Recently, the use of the semiconducting single walled carbon nanotube is more complex. Various electronic devices such as OLED driving circuit [134],[135] logic circuit [136],[137], active matrix for pressure sensor array[138]−[139], and X−ray imager [140] are tried using the semiconducting material. Although some technical issues are remained, the semiconducting single walled carbon nanotube is the most useful and versatile materials in next−generation electronics.

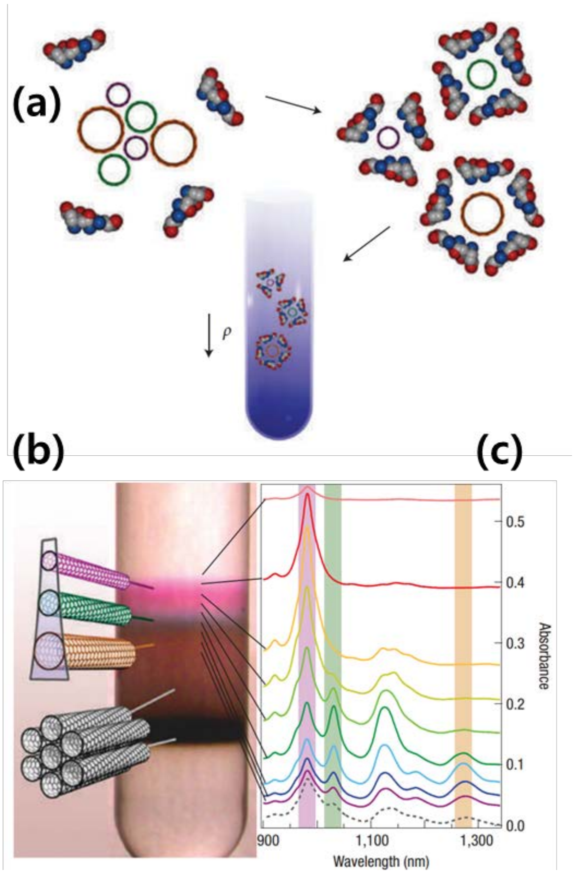


Fig. 1.5 A General approach for sorting carbon nanotube by electronic type that consists of metallic and semiconducting carbon nanotube. (a) Schematic image of the separation process exhibits surfactant encapsulation on the carbon nanotube and different density determined by diameter of carbon nanotube (b) Optical image of the separated solution by ultracentrifugation (c) Optical absorbance of the separated solution

1.5.3 Energy storage device

Energy storage is a question of long standing in the electronic device application for the use in a certain area where power supply is limited. The energy storage devices are classified by the mechanism during charging–discharging. While pseudo–capacitor based on the redox mechanism of metal oxide materials has high energy density and is more suitable for large scale electronics such as battery, supercapacitor (is also called as ultracapacitor) based on the electrical double layer mechanism has high power density and high charging speed. [141] The supercapacitor requires high surface area to increase contact between electrode and ions in electrolyte during chaging–discharging process. Carbon materials are well–known materials for high surface area, and carbon nanotube is also one of the promising candidates for supercapacitor. [142] Although the efforts on surface area of carbon nanotube for improving energy density is also studied using fractured carbon nanotube, many interests for carbon nanotube–based supercapacitor are focused on specific substrate recently. To use the supercapacitor for flexible or stretchable electronics devices, various substrates such as paper [143], cotton [144], textile [145], and PDMS [72] have been studied. Especially, high porous structure of cotton and textile benefit the net surface area of the system; this leads to high power and energy density of supercapacitor with high charging speed. The development on the substrate will enable to obtain stretchable energy storage device with high performance.

Reference

[1] S. Iijima, “Helical microtubules of graphitic carbon” Nature, vol. 354, pp. 56−58, 1991

[2] C. L. Cheung, A. Kurtz, H. Park, and C. M. Lieber, “Diameter−Controlled Synthesis of Carbon nanotubes” J. Phys. Chem. B, vol. 106, pp. 2429−2433, 2002

[3] H. W. Zhu, C. L. Xu, D. H. Wu, B. Q. Wei, R. Vajtal, and P. M. Ajayan, “Direct Synthesis of Long Single−Walled Carbon Nanotube Strands” Science, vol. 296, pp. 884−886, 2002

[4] R. Sengupta, M. Bhattacharya, S. Bandyopadhyay, and A. K. Bhowmick, “A review on the mechanical and electrical properties of graphite and modified graphite reinforced polymer composites" Prog. Polym. Sci., vol. 36, pp. 638−670, 2011

[5] T. W. Ebbesen, H. J. Lezec, H. Hiura, J. W. Bennettm, H. F. Ghaemi, and T. Thio, “Electrical conductivity of individual carbon nanotubes”, Nature, vol. 382, pp. 54−56, 1996

[6] M. J. O’ Connell, S. M. Bachilo, C. B. Huffman, V. C. Moore, M. S. Strano, E. H. Haroz, K. L. Rialo, P. J. Boul, W. H. Noon, C. Kittrell, J. Ma, R. H. Hauge, R. B. Weisman, and R. E. Smalley, “Band Gap

Fluorescence from Individual Single−Walled Carbon Nanotubes” Science, vol. 297, pp. 593−596, 2002

[7] K. H. An, W. S. Kim, Y. S. Park, Y. C. Choi, S. M. Lee, D. C. Chung, D. J. Bae, S. C. Lim, and Y. H. Lee, “Supercapacitors Using Single−Walled Carbon Nanotube Electrodes” Adv. Mater., vol. 7, pp. 497−500, 2001

[8] K. H. An, W. S. Kim, Y. S. Park, J. −M. Moon, D. J. Bae, S. C. Lim, Y. S. Lee, and Y. H. Lee “Electrochemical Properties of High−Power Supercapacitors Using Single−Walled Carbon Nanotube Electrodes” Adv. Funct. Mater., vol. 11, pp. 387−392, 2001

[9] D. Zhang, K. Ryu, X. Liu, E. Polikarpov, J. Ly, M. E. Tompson, and C. Zhou, “Transparent, Conductive, and Flexible Carbon Nanotube Films and Their Application in Organic Light−Emitting Diodes” Nano Lett., vol. 6, pp. 1880−1886, 2006

[10] A. D. Pasquier, H. E. Unalan, A. Kanwal, S. Miller, and M. Chhowalla, “Conducting and transparent single−wall carbon nanotube electrodes for polymer−fullerene solar cells” Appl. Phys. Lett., vol. 87, 203511 (3pp), 2005

[11] M. C. LeMieux, M. Roberts, S. Barman, Y. W. Jin, J. M. Kim,

and Z. Bao, "Self−Sorted, Aligned Nanotube Networks for Thin−Film Transistors" Science, vol. 321, pp. 101−104, 2008

[12] N. Rouhi, D. Jain, K. Zand, and P. J. Burke, "Fundamental Limits on the Mobility of Nanotube−Based Semiconducting Inks" Adv. Mater., vol. 23, pp. 94−99, 2001

[13] J. Li, Y. Lu, Q. Ye, M. Cinke, J. Han, and M. Meyyappan, "Carbon Nanotube Sensors for Gas and Organic Vapor Detection" Nano Lett, vol. 3, pp. 929−933, 2003

[14] N. Sinha, J. Ma, and J. T. W. Yeow, "Carbon Nanotube−Based Sensors" J. Nanosci. Nanotechnol., vol. 6, pp. 573−590, 2006

[15] C. Stampfer, T. Helbling, D. Obergfell, B. Schoberle, M. K. Tripp, A. Jungen, S. Roth, V. M. Bright, and C. Hierold, "Fabrication of Single−Walled Carbon−Nanotube−Based Pressure Sensors" Nano Lett., vol. 6, pp. 233−237, 2006

[16] B. T. Kelly, "Physics of Graphite" Applied Science, London, 1981

[17] P. M. Ajayan, "Nanotubes from Carbon" Chem. Rev., vol. 99, pp. 1787−1799, 1999

[18] R. W. G. Wyckoff, "Crystal Structure", Interscience, New York, 1964

[19] B. I. Dunlap, “Connecting carbon tubules”, Phys. Rev. B, vol. 46, pp. 1933–1936, 1992

[20] R. Saito, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, “Electronic structure of graphene tubules based on C_{60}” Phys. Rev. B, vol. 46, pp. 1804–1811, 1991

[21] M. S. Dresselhaus, G. Dresselhaus, and R. Saito, “Physics of carbon nanotubes” carbon, vol. 33, pp. 883–891, 1995

[22] A. H. C. Neto, F. Guinea, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, “The electronic properties of graphene” Rev. Mod. Phys., vol. 81, pp. 109–162, 2009

[23] M. J. Allen, V. C. Tung, and R. B. Kaner, “Honeycomb Carbon: A Review of Graphene” Chem. Rev., vol. 110, pp. 132–145, 2010

[24] M. S. Fuhrer, J. Nygard, L. Shih, M. Forero, Y. –G. Yoon, M. S. C. Mazzoni, H. J. Choi, J. Ihm, S. G. Louie, A. Zetti, and P. L. McEuen, “Crossed Nanotube Junctions” Science, vol. 288, pp. 494–497, 2000

[25] R. Saito, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, “Electronic structure of chiral graphene tubules” Appl. Phys. Lett., vol. 60, 2204 (3pp), 1992

[26] R. Saito, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, “Electronic structure and growth mechanism of carbon tubules” Mater. Sci. Eng. B, vol. 19, pp. 185-191, 1993

[27] M. S, Dresselhaus, G. Dresselhaus, and P. Avouris, “Carbon nanotubes: Synthesis, Structure, Properties, and Application” Springer, New York, 2001

[28] M. B. Nardelli, B. I. Yakobson, and J. Bernholc, “Brittle and Ductile Behavior in Carbon Nanotubes” Phys. Rev. Lett., vol. 81, pp. 4656-4659, 1998

[29] A. Rochefort, P. Avouris, F. Lesage, D. R. Salahub, “Electrical and mechanical properties of distorted carbon nanotubes” Phys. Rev. B, vol. 60, 13824 (7pp), 1999

[30] J. W. G. Wilder, L. C. Venema, A. G. Rinzler, R. E. Smalley, and C. Dekker, “Electronic structure of atomically resolved carbon nanotubes”, Nature, vol.391, pp. 59-62, 1997

[31] O. Gulseren, T. Yildirim, S. Ciraci, and C. Kilic, “Reversible band-gap engineering in carbon nanotubes by radial deformations” Phys. Rev. B, vol. 65, 155410 (7pp), 2002

[32] C. Zhou, J. Kong, E. Yenilmez, and H. Dai “Modulated Chemical Doping of Individual Carbon Nanotubes” Science, vol.

290, pp. 1552−1555, 2000

[33] R. Saito, G. Dresselhaus, and M. S. Dresselhaus, “Physical Properties of Carbon Nanotubes” Imperial College Press, London, 1998

[34] M. S. Dresselhaus, G. Dresselhaus, R. Saito, and A. Jorio, “Raman spectroscopy of carbon nanotubes” Physics Reports, vol. 409, pp. 47−99, 2005

[35] S. M. Bachilo, M. S. Strano, C. Kittrell, R. H. Hauge, R. E. Smalley, and R. B. Weisman, “Structure−Assigned Optical Spectra of Single−Walled Carbon Nanotubes” Science, vol. 298, pp. 2361−2366, 2002

[36] C. T. White, D. H. Robertson, and J. W. Mintmire, “Helical and rotational symmetries of nanoscale graphitic tubules” Phys. Rev. B, vol. 47, pp. 5485−5488, 1992

[37] S. Bandow and S. Asaka, “Effect of the Growth Temperature on the Diameter Distribution and Chirality of Single−Wall Carbon Nanotubes” Phys. Rev. Lett., vol. 80, pp. 3779−3782, 1998

[38] V. Sazonova, Y. Yaish, H. Ustunel, D. Roundy, T. A. Arias, and P. L. McEuen, “A tunable carbon nanotube electromechanical oscillator” Nature, vol. 431, pp. 284−287, 2004

[39] R. Martel, T. Schmidt, H. R. Shea, T. Hertel, and Ph Avouris, “Single− and multi−wall carbon nanotube field−effect transistors” Appl. Phys. Lett., vol. 73, 2447 (3pp), 1998

[40] S. Park, M. Vosguerichian, and Z. Bao, “A review of fabrication and applications of carbon nanotube film−based flexible electronics” Nanoscale, vol. 5, pp. 1727−1752, 2013

[41] C. Wang, J. Zhang, K. Ryu, A. Badmaev, L. G. D. Arco, and C. Zhou, “Wafer−Scale Fabrication of Separated Carbon Nanotube Thin−Film Transistors for Display Applications” Nano Lett., vol. 9, pp. 4285−4291, 2009

[42] S. G. Rao, L. Huang, W. Setyawan, and S. Hong, “Nanotube electronics: Large−scale assembly of carbon nanotubes” Nature, vol. 425, pp. 36−37, 2003

[43] Q. Cao, H. -S. Kim, N. Pimparkar, J. P. Kulkarni, C. Wang, M. Shim, K. Roy, M. A. Alam, and J. A. Rogers, “Medium−scale carbon nanotube thin film integrated circuits on flexible plastic substrate" Nature, vol. 454, pp. 495−500, 2008

[44] P. H. Lau, K. Takei, C. Wang, Y. Ju, J. Kim, Z. Yu, T. Takahashi, G. Cho, and A. Javey, “Fully Printed, High Performance Carbon Nanotube Thin−Film Transistors on Flexible Substrates”,

Nano Lett., vol. 13, pp. 3864–3869, 2013

[45] L. Hu, D. S. Hecht, and G. Gruner, “Carbon Nanotube Thin Films: Fabrication, Properties, and Applications” Chem. Rev., pp. 5790–5844, 2010

[46] H. –Z. Geng., K. K. Kim, K. P. So, Y. S. Lee, Y. Chang, and Y. H. Lee, “Effect of Acid Treatment on Carbon Nanotube–Based Flexible Transparent Conducting Films” , J. Am. Chem. Soc., vol. 129, pp. 7758–7759, 2007

[47] R. Graupner, J. Abraham, A. Vencelova, T. Seyller, F. Hennrich, M. M. Kappes, A. Hirsch, and L. Ley, “Doping of single–walled carbon nanotube bundles by Bronsted acids” Phys. Chem. Chem. Phys, vol. 5, pp. 5472–5476, 2003

[48] H. Kong, C. Gao, and D. Yan, “Controlled Functionalization of Multiwalled Carbon Nanotubes by in Situ Atom Transfer Radical Polymerization” J. Am. Chem. Soc., vol. 126, pp. 412–413, 2004

[49] M. S. Strano, C. A. Dyke, M. L. Usrey, P. W. Barone, M. J. Allen, H. Shan, C. Kittrell, R. H. Hauge, J. M. Tour, and R. E. Smalley, “Electronic Structure Control of Single–Walled Carbon Nanotube Functionalization” Science, vol. 301, pp. 1519–1522, 2003

[50] T. Takenobu, T. Takano, M. Shiraishi, Y. Murakami, M. Ata, H. Kataura, Y. Achiba, and Y. Iwasa, “Stable and controlled amphoteric doping by encapsulation of organic molecules inside carbon nanotubes”, Nat. Mater., vol. 2, pp. 683−688, 2003

[51] D. S. Hecht, L. Hu, and G. Irvin, “Emerging Transparent Electrodes Based on Thin Films of Carbon Nanotubes, Graphene, and Metallic Nanostructures” Adv. Mater., vol. 23, pp. 1482−1513, 2011

[52] L. Hu, H. S. Kim, J. -Y. Lee, P. Peumans, and Y. Cui, “Scalable Coating and Properties of Transparent, Flexible, Silver Nanowire Electrodes” ACS Nano, vol. 4, pp. 2955−2963, 2010

[53] K. Jiang, A. Eitan, L. S. Schadler, P. M. Ajayan, and R. W. Siegel, “Selective Attachment of gold Nanoparticles to Nitrogen−doped Carbon Nanotubes”, Nano Lett., vol. 3, pp. 275−277, 2003

[54] K. Y. Chun, Y. Oh, J. Rho, J. -H. Ahn, Y. -J. Kim, H. R. Choi, and S. Baik “Highly conductive, printable and stretchable composite films of carbon nanotubes and silver” Nat. Nanotechnol., vol. 5, pp. 853−857, 2010

[55] T. Araki, M. Nogi, K. Suganuma, M. Kogure, and O. Kirihara, “Printable and Stretchable Conductive Wirings Comprising Silver

Flakes and Elastomers” IEEE Elec. Dev. Lett., vol. 32, pp. 1424–1426, 2011

[56] M. M. J. Treacy, T. W. Ebbesen, and J. M. Gibson, “Exceptionally high Young’s modulus observed for individual carbon nanotubes” Nature, vol. 381, pp. 678–680, 1996

[57] M. –F. Yu, O. Lourie, M. J. Dyer, K. Moloni, T. F. Kelly, and R. S. Ruoff, “Strength and Breaking Mechanism of Multiwalled Carbon Nanotubes Under Tensile Load” Science, vol. 287, pp. 637–640, 2000

[58] M. Meo, M. Rossi, “Prediction of Young’s modulus of single wall carbon nanotubes by molecular–mechanics based finite element modelling” Compos. Sci. Technol., vol. 66, pp. 1597–1605, 2006

[59] S. B. Sinnott and R. Andrews, “Carbon Nanotubes: Synthesis, Properties, and Applications” Critical Reviews in Solid State and Materials Science, vol. 26, pp. 145–249, 2001

[60] M. –F. Yu, B. S. Files, S. Arepalli, and R. S. Ruoff “Tensile Loading of Ropes of Single Wall Carbon Nanotubes and their Mechanical Properties” Phys. Rev. Lett., vol. 84, pp. 5552–5555, 2000

[61] F. Li, H. M. Cheng, S. Bar, G. Su, and M. S. Dresselhaus, “Tensile strength of single−walled carbon nanotubes directly measured from their macroscopic ropes” Appl. Phys. Lett., vol. 77, 3161 (3pp), 2000

[62] M. S. K. −Gdoutos, Z. S. Metaxa, and S. P. Shah, “Highly dispersed carbon nanotube reinforced cement based materials” Cem. Con. Res., vol. 40, pp. 1052−1059, 2010

[63] A. Sobolkina, V. Mechtcherine, V. Khavrus, D. Maier, M. Mende, M. Ritschel, and A. Leonhardt, “Dispersion of carbon nanotubes and its influence on the mechanical properties of the cement matrix” , Cem. Con. Com., vol. 34, pp. 1104−1113, 2012

[64] G. −D. Zhan, J. D. Kuntz, J. Wan, and A. K. Mukherjee, “Single−wall carbon nanotubes as attractive toughening agents in alumina−based nanocomposites” Nat. Mater., vol. 2, pp. 38−42, 2003

[65] R. Haggenmueller, H. H. Gommans, A. G. Rinzler, J. E. Fisher, and K. I. Winey, “Alighned single−wall carbon nanotubes in composites by melt processing methods” Chem. Phys. Lett, vol. 330, pp. 219−225, 2000

[66] B. Vigolo, A. Penicaud, C. Coulon, C. Sauder, R. Pailler, C.

Journet, P. Bernier, and P. Poulin, “Macroscopic Fibers and Ribbons of Oriented Carbon Nanotubes” Science, vol. 290, pp. 1331–1334, 2000

[67] A. Mamedov, N. A. Kotov, M. Prato, D. M. Guldi, J. P. Wicksted, and A. A. Hirsch, “Molecular design of strong single–wall carbon nanotube/polyelectrolyte multilayer composites” , Nat. Mater., vol. 1, pp. 190–194, 2002

[68] W. Xue and T. Cui, “Characterization of layer–by–layer self–assembled carbon nanotube multilayer thin films” , Nanotechnology, vol. 18, 145709 (7pp), 2007

[69] B. S. Shim, Z. Tang, M. P. Morabito, A. Agarwal, H. Hong, and N. A. Kotov, “Integration of Conductivity, Transparency, and Mechanical Strength into Highly Homogeneous Layer–by–Layer Composites of Single–Walled Carbon Nanotubes for Optoelectronics” Chem. Mater., vol. 19, pp. 5467–5474, 2007

[70] D. Tahk, H. H. Lee, and D. –Y. Khang, “Elastic Moduli of Organic Electronic Materials by the Buckling Method” , Macromolecules, vol. 42, pp. 7079–7083, 2009

[71] C. M. Stafford, C. Harrison, K. L. Beers, A. Karim, E. J. Amis, M. R. VanLandingham, H. –C. Kim, W. Volksen, R. D. Miller, and E.

E. Simony, “A buckling-based metrology for measuring the elastic moduli of polymer thin films” Nat. Mater., vol. 3, pp. 545-550, 2004

[72] Z. Niu, H. Dong, B. Zhu, J. Li, H. H. Hng, W. Zhou, X. Chen, and S. Xie, “Highly Stretchable, Integrated Supercapacitors Based on Single-Walled Carbon Nanotube Films with Continuous Reticulate Architecture” Adv. Mater., vol. 25, pp. 1058-1064, 2013

[73] D. J. Lipomi, B. C. -K. Tee, M. Vosgueritchian, and Z. Bao, “Stretchable Organic Solar Cells”, Adv. Mater., vol. 23, pp. 1771-1775, 2011

[74] T. Yamada, Y. Hayamizu, Y. Yamamoto, Y. Yomogida, A. I. -Najafabadi, D. N. Futaba, and K. Hata, “A Stretchable carbon nanotube strain sensor for human-motion detection” Nat. Nanotechnol., vol. 6, pp. 296-301, 2011

[75] D. J. Lipomi, M. Vosgueritchian, B. C. -K. Tee, S. L. Hellstrom, J. A. Lee, C. H. Fox, and Z. Bao, “Skin-like pressure and strain sensors based on transparent elastic films of carbon nanotubes”, Nat. Nanotechnol., vol. 6, pp. 788-792, 2011

[76] X. Li, R. Zhang, W. Yu, K. Wang, J. Wei, D. Wu, A. Cao, Z. Li, Y. Cheng, Q. Zheng, R. S. Ruoff, and H. Zhu, “Stretchable and highly

sensitive graphene−on−polymer strain sensors” , vol. 2, 870 (6pp), 2012

[77] T. Pichler, M. Knupfer, M. S. Golden, and J. Fink, "Localized and Delocalized Electronic states in Single−Wall Carbon Nanotube" Phys. Rev. Lett., vol. 80, pp. 4729−4732, 1998

[78] H. Katura, Y. Kumazawa, Y. Maniwa, I. Umezu, S. Suzuki, Y. Ohtsuka, and Y. Achiba, “Optical properties of Single−wall Carbon Nanotubes” , Synth. Met., pp. 2555−2558, 1999

[79] L. Hu, D. S. Hecht, and G. Gruner, “Percolation in Transparent and Conducting Carbon Nanotube Network” Nano Lett., vol. 4, pp. 2513−2517, 2004

[80] E. Artukovic, M. Kaempgen, D. S. Hecht, S. Roth, and G. Gruner, "Transparent and Flexible Carbon Nanotube Transisors” Nano Lett, vol. 5, pp. 757−760, 2005

[81] G. Gruner, “Carbon nanotube films for transparent and plastic electronics” , J. Mater. Chem., vol. 16, pp. 3533−3539, 2006

[82] K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J. −H. Ahn, P. Kim, J. −Y. Choi, and B. H. Hong, “Large−scale pattern growth of graphene films for stretchable transparent electrodes”

Nature, vol. 457, pp. 706−710, 2009

[83] S. Bae, H. Kim, Y. Lee, X. Xu, J. -S. Park, Yi. Zheng, J. Balakrishnan, T. Lei, H. R. Kim, Y. I. Song, Y. -J. Kim, K. S. Kim, B. Ozyilmaz, J. -H. Ahn, B. H. Hong, and S. Iijima, "Roll−to−roll production of 30−inch graphene films for transparent electrodes" Nat. Nanotechnol., vol. 5, pp. 574−578, 2010

[84] J. Home, M. Whitney, C. Piskoti, and A. Zetti, "Thermal conductivity of single−walled carbon nanotubes" Phys. Rev. B, vol. 59, pp. R2514−R2516, 1999

[85] W. Yi. L. Lu, Z. D.−lin, Z. W. Pan, and S. S. Xie, "Linear specific heat of carbon nanotubes" Phys. Rev. B, vol. 59, pp. R9015−R9018, 1999

[86] S. Berber, Y. -K. Kwon, and D. Tomanek, "Unusually High Thermal Conductivity of Carbon Nanotubes" Phys. Rev. Lett., vol. 84, pp. 4613−4616, 2000

[87] M. Meyyanppan, L. Delzeit, A. Cassell, and D. Hash, "Carbon nanotube growth by PECVD: a review" Plasma Sources Sci. Technol., vol. 12, pp. 205−216, 2003

[88] O. Matarredona, H. Rhoads, Z. Li, J. H. Harwell, L. Balzano, and D. E. Resasco, "Dispersion of Single−Walled Carbon

Nanotubes in Aqueous Solutions of the Anionic Surfactant NaDDBS" J. Phys. Chem. B, vol. 107, pp. 13357−13367, 2003

[89] P. J. Boul, J. Liu, E. T. Mickelson, C. B. Huffman, L. M. Ericson, I. W. Chiang, K. A. Smith, D. T. Colbert, R. H. Hauge, J. L. Margrave, and R. E. Smalley, "Reversible sidewall functionalization of buckytubes" Chem. Phys. Lett., vol. 310, pp. 367−372, 1999

[90] K. D. Ausman, R. Piner, O. Lourie, M. Korobov, and R. S. Ruoff, "Organic Solvent Dispersion of Single−Walled Carbon Nanotubes: Toward Solutions of Pristine Nanotubes" J. Phys. Chem. B, vol. 104, pp. 8911−8915, 2000

[91] D. Carponcin, E. Dantras, G. Aridon, F. Levallois, L. Cadiergues, and C. Lacabanne, "Evolution of dispersion of carbon nanotubes in Polyamide 11 matrix composites as determined by DC conductivity" Compos. Sci. Tech., vol. 72, pp. 515−520, 2012

[92] T. Kyrklund, P. Kjellstrand, and K. Haglid, "Brain lipid changes in rats exposed to xylene and toluene" Toxicology, vol. 45, pp. 123−133, 1987

[93] J. Liu, A. G. Rinzler, H. Dai, J. H. Hafner, R. K. Bradley, P. J. Boul, A. Lu, T. Iverson, K. Shelimov, C. B. Huffman, F. R. −Macias, Y. −S. Shon, T. R. Lee, D. T. Colbert, and R. E. Smalley,

“Fullerene Pipers” Science, vol. 280, pp. 1253−1256, 1998

[94] V. Krstic, G. S. Duesberg, J. Muster, M. Burghard, and S. Roth, “Langmuir−Blodgett Films of Matrix−Diluted Single−Walled Carbon Nanotubes” Chem Mater.. vol. 10, pp. 2338−2340, 1998

[95] V. C. Moore, M. S. Strano, E. H. Haroz, R. H. Hauge, and R. E. Smalley “Individually Suspended Single−Walled Carbon Nanotubes in Various Surfactants” Nano Lett., vol. 3, pp. 1379−1382, 2003

[96] L. Jiang, L. Gao, and J. Sun, “Production of aqueous colloidal dispersions of carbon nanotubes” , J. Colloid. Interface Sci., vol. 260, pp. 89−94, 2003

[97] M. F. Islam, E. Rojas, D. M. Bergey, A. T. Johnson, and A. G. Yodh, “High Weight Fraction Surfactant Solubilization of Single−Wall Carbon Nanotubes in Water” Nano Lett., vol. 3, pp. 269−273, 2003

[98] J. L. Blackburn, T. M. Barnes, M. C. Beard, Y. −H. Kim, R. C. Tenent, T. J. Mcdonald, B. To, T. J. Coutts, and J. Heben, “Transparent Conductive Single−Walled Carbon Nanotube Networks with Precisely Tunable Ratios of Semiconducting and Metallic Nanotubes” ACS Nano, vol. 2, pp. 1266−1274, 2008

[99] H. Tantang, J. Y. Ong, C. L. Loh, X. Dong, P. Chen, Y. Chen, X.

Hu, L. P. Tan, and L. -J. Li, “Using oxidation to increase the electrical conductivity of carbon nanotube electrodes” Carbon, vol. 47, pp. 1867−1885, 2009

[100] H. -Z. Geng, D. S. Lee, K. K. Kim, G. H. Han, H. K. Park, and Y. H. Lee, “Absorption spectroscopy of surfactant−dispersed carbon nanotube film: Modulation of electronic structures” Chem. Phys. Lett., vol. 455, pp. 275−278, 2008

[101] H. C. Schniepp, J. -L. Li, M. J. McAllister, H. Sai, M. H. -Alonso, D. H. Adamson, R. K. Prud’ homme, R. Car, D. A. Saville, and I. A. Aksay, “Functionalized Single Graphene Sheets Derived from Splitting Graphite Oxide” J. Phys. Chem. B, vol. 110, pp. 8535−8539, 2006

[102] H. Ago, T. Kugler, F. Cacialli, W. R. Salaneck, M. S. P. Shaffer, A. H. Windle, and R. H. Friend, “Work Functions and Surface Functional Groups of Multiwall Carbon Nanotubes” J. Phys, Chem B, vol. 103, pp. 8116−8121, 1999

[103] A. Garg and S. B. Sinnott, “Effect of chemical functionalization on the mechanical properties of carbon nanotubes” Chem. Phys. Lett., vol. 295, pp. 273−278, 1998

[104] P. M. Ajayan, O. Stephan, C. Colliex, and D. Trauth,

"Aligned Carbon Nanotube Arrays Formed by Cutting a Polymer Resin−Nanotube Composite" Science, vol. 265, pp. 1212−1214, 1994

[105] B. P. Grady, "Carbon nanotube−polymer composites" Wiley, New Jersey, 2011

[106] P. Andrews and M. C. Weisenberger, "Carbon nanotube polymer composites" Current Opinion in Solid State and Materials Science, vol. 8, pp. 31−37, 2004

[107] Z. Spitalsky, D. Tasis, K. Papagelis, and C. Galiotis, "Carbon nanotube−polymer composites: Chemistry, processing, mechanical and electrical properties" Prog. Polym. Sci., vol. 35, pp. 357−401, 2010

[108] J. N. Coleman, U. Khan, W. J. Blau, Y. K. Gun' ko, "Small but strong: A review of the mechanical properties of carbon nanotube−polymer composites" Carbon, vol. 44, pp. 1624−1652, 2006

[109] L. Ci, J. Suhr, V. Pushparaj, X. Zhang, and P. M. Ajayan, "Continuous Carbon Nanotube Reinforced Composites" Nano Lett., pp. 2762−2766, 2008

[110] K. H. Kim, M. Vural, and M. F. Islam, "Single−Walled

Carbon Nanotube Aerogel-Based Elastic Conductors” Adv. Mater., vol. 23, pp. 2865-2869, 2011

[111] J. A. Rogers, T. Someya, and Y. Huang, “Materials and Mechanics for Stretchable Electronics” Science, vol. 327, pp. 1603-1607, 2010

[112] T. Sekitani and T. Someya, “Stretchable, Large-area Organic Electronics” Adv. Mater., vol. 22, pp. 2228-2246, 2010

[113] I. M. Graz, D. P. J. Cotton, A. Robinson, and S. P. Lacour, “Silicone substrate with in situ strain relief for stretchable thin-film transistors”, Appl. Phys. Lett., vol. 98, 124101 (3pp) 2011

[114] T. Sekitani, Y. Noguchi, K. Hata, T. Fukushima, T. Aida, and T. Someya, “A Rubberlike Stretchable Active Matrix Using Elastic Conductors” Science, vol. 321, pp. 1468-1472, 2008

[115] T. Sekitani, H. Nakajima, H. Maeda, T. Fukushima, T. Aida, K. Hata, and T. Someya, “Stretchable active-matrix organic light-emitting diode display using printable elastic conductors” Nat. Mater., vol. 8, pp. 494-499, 2009

[116] X. Wang, T. Li, J. Adams, and J. Yang, “Transparent, stretchable, carbon-nanotube-inlaid conductors enabled by standard replication technology for capacitive pressure, strain and

tough sensors" J. Mater. Chem. A, vol. 1, pp. 3580−3586, 2013

[117] L. Li, Z. Yang, H. Gao, H. Zhang, J. Ren, X. Sun, T. Chen, H. G. Kia, and H. Peng, "Vertically Aligned and Penetrated Carbon Nanotube/Polymer Composite Film and Promising Electronic Application" Adv. Mater., vol. 23, pp. 3730−3735, 2011

[118] H. Liu, M. Li, O. Voznyy, L. Hu, Q. Fu, D. Zhoum Z. Xia, E. H. Sargent, and J. Tang, "Physically Flexible, Rapid−Response Gas Sensor Based on Colloidal Quantum Dot Solids" Adv. Mater., vol. 26, pp. 2718−2724, 2014

[119] H. E. Holling, H. C. Boland, and E. Russ, "Investigation of arterial obstruction using a mercury−in−rubber strain gauge" Am. Heart. J., vol. 62, pp. 194−205, 1961

[120] B. J. Munro, T. E. Campbell, G. G. Wallace, and J. R. Steele, "The intelligent knee sleeve: A wearable biofeedback device" Sensors and Actuators B, vol. 131, pp. 541−547, 2008

[121] M. Liu, D. M. Frangopol, and S. Kim, "Bridge Safety Evaluation Based on Monitored Live Load Effects", J. Bridge Eng., vol. 14, pp. 257−269, 2009

[122] V. Arumugam, M. D. Naresh, and R. Sanjeevi, "Effect of strain rate on the fracture behavior of skin", J. Biosci., vol. 19, pp.

307–313, 1994

[123] C. H. Daly, and G. F. Odland, “Age–related Changes in the Mechanical Properties of Human Skin” J. Invest. Dermatol., vol. 73, pp. 84–87, 1979

[124] C. Mattmann, F. Clemens, and G. Troster, “Sensor for Measuring Strain in Textile” Sensors, vol. 8, pp. 3719–3732, 2008

[125] M. Hempel, D. Nezichm, J. Kong, and M. Hofmann, “A Novel Class of Strain Gauges Based on Layered Percolative Films of 2D Materials”, Nano Lett., vol. 12, pp. 5714–5718, 2012

[126] L. Cai, L. Song, P. Luan, Q. Zhang, N. Zhang, Q. Gao, D. Zhao, Z. Zhang, M. Tu, F. Yang, W. Zhou, Q. Fan, J. Luo, W. Zhou, P. M. Ajayan, and S. Xie “Super–stretchable, Transparent Carbon Nanotube–Based Capacitive Strain Sensors for Human Motion Detection” Scientific Reports, vol. 3, 3048 (8pp), 2013

[127] M. A. Topinka, M. W. Rowell, D. G.–Gordon, M. D. McGehee, D. S. Hecht, and G. Gruner, “Charge Transport in Interpenetrating Networks of Semiconducting and Metallic Carbon Nanotubes, Nano Lett., vol. 9, pp. 1866–1871, 2009

[128] T. Tanaka, H. Jin, Y. Miyata, S. Fujii, H. Suga, Y. Naitoh, T.

Minari, T. Miyadera, K. Tsukagoshi, and H. Kataura, “Simple and Scalable Gel−Based Separation of Metallic and Semiconducting Carbon Nanotubes” Nano Lett., vol. 9, pp. 1497−1500

[129] D. –M. Sun, M. Y. Timmermans, Y. Tian, A. G. Nasibulin, E. I. Kauppinen, S. Kishimoto, T. Mizutani, and Y. Ohno, “Flexible high−performance carbon nanotube integrated circuits” Nat. Nanotechnol., vol. 6, pp. 156−161, 2011

[130] D. Chattopadhyay, I Galeska, and F. Papadimitrakopoulos, “A Route for Bulk Separation of Semiconducting from Metallic Single−Wall Carbon Nanotubes”, vol. 125, pp. 3370−3375, 2003

[131] M. S. Arnold, A. A. Green, J. F. Hulvat, S. I. Stupp, and M. C. Hersam, “Sorting carbon nanotubes by electronic structure using density differentiation” Nat. Nanotechnol., vol. 1, pp. 60−65, 2006

[132] S. –J. Choi, C. Wang, C. C. Lo, P. Bennett, A. Javey, and J. Bokor, “Comparative study of solution−processed carbon nanotube network transistors” Appl. Phys. Lett., vol. 101, 112104 (4pp), 2012

[133] M. C. LeMieux, S. Sok, M. E. Roberts, J. P. Opatkiewicz, D. Liu, S. N. Barman, N. Patil, S. Mitra, and Z. Bao, “Solution Assembly of Organized Carbon Nanotube Networks for Thin−Film

Transistors" ACS NANO, vol. 3, pp. 4089−4097, 2009

[134] P. Chen, Y. Fu, R. Aminirad, C. Wang, J. Zhang, K. Wang, K. Galatsis, and C. Zhou, "Fully Printed Separated Carbon Nanotube Thin Film Transistor Circuits and Its Application in Organic Light Emitting Diode Control" Nano Lett., vol. 11, pp. 5301−5308, 2011

[135] J. Zhang, Y. Fu, C. Wang, P. –C. Chen, Z. Liu, W. Wei, C. Wu, M. E. Thompson, and C. Zhou, "Separated Carbon Nanotube Macroelectronics for Active Matrix Organic Light−Emitting Diode Displays" Nano Lett., vol. 11, pp. 4852−4858, 2011

[136] S. Y. Lee, S. W. Lee, S. M. Kim, W. J. Yu, Y. W. Jo, and Y. H. Lee, "Scalable Complementary Logic Gates with Chemically Doped Semiconducting Carbon Nanotube Transistors" ACS NANO, vol. 5, pp. 2369−2375, 2011

[137] M. Ha, Y. Xia, A. A. Green, W. Zhang, M. J. Renn, C. H. Kim, M. C. Hersam, and C. D. Frisbie, "Printed, Sub−3V Digital Circuits on Plastic From Aqueous Carbon Nanotube Inks" ACS NANO, vol. 4, pp. 4388−4395, 2010

[138] C. Wang, D. Hwang, Z. Yu, K. Takei, J. Park, T. Chen, B. Ma, and A. Javey, "User−interactive electronic skin for instantaneous pressure visualization" Nat. Mater., vol. 12, pp. 899−904, 2013

[139] T. Takahashi, K. Takei, A. G. Gillies, R. S. Fearing, and A. Javey, “Carbon Nanotube Active-Matrix Backplanes for Conformal Electronics and Sensors” Nano Lett., vol. 11, pp. 5408-5413, 2011

[140] T. Takahashi, Z. Yu, K. Chen, D. Kiriya, C. Wang, K. Takei, H. Shiraki, T. Chen, B. Ma, and A. Javey, “Carbon Nanotube Active-Matrix Backplanes for Mechanically Flexible Visible Light and X-ray Imagers” Nano Lett., vol. 13, pp. 5425-5430, 2013

[141] G. Wang, L. Zhang, and J. Zhang, “A review of electrode materials for electrochemical supercapacitors” Chem. Soc. Rev, vol. 41, pp. 797-828, 2012

[142] M. F. L. D. Volder, S. H. Tawfick, R. H. Baughman, and A. J. Hart, “Carbon Nanotubes: Present and Future Commercial Application” Science, vol. 339, pp. 535-539, 2013

[143] L. Hu, H. WU, and Y. Cui, “Printed energy storage devices by integration of electrodes and separators into single sheets of paper” Appl. Phys. Lett., vol. 96, 183502 (3pp), 2010

[144] L. Hu, M. Pasta, F. L. Mantia, L. Cui, S. Jeong, H. D. Deshazer, J. W. Choi, S. M. Han, and Y. Cui, “Stretchable, Porous, and Conductive Energy Textiles” Nano Lett., vol. 10, pp. 708-714,

2010

[145] L. Hu, W. Chen, X. Xie, N. Lium Y. Yang, H. Wu, Y. Yao, M. Pasta, H. N. Alshareef, and Y. Cui, “Symmetrical MnO2−Carbon Nanotube−Textile Nanostructures for Wearable Pseudocapacitors with High Mass Loading” , ACS Nano, vol. 5, pp. 8904−8913, 2011

[146] S. Banerjee, T. H. -Benny and S. S. Wong, “Covelent Surface Chemistry of Single−Walled Carbon Nanotubes” Adv. Mater., vol. 17, pp. 17−29, 2005

Chapter 2

Synthesis of single-walled carbon nanotube ink in aqueous solvent and optimization of printing conditions for inkjet-printed SWCNT thin film

2.1 Introduction

Recently, scalability in fabrication process should be considered for low process cost and large scale device. There are many researches for the scalability of fabrication process; a solution process is one of the promising candidates for the technical issues. In fact, many processes in industrial process have been substituted to the solution process due to the scalability. Although high-performance devices such as memory, central processing unit are still difficult to be fabricated by the solution process, simple devices have been tried using the method. When the solution process is optimized, various printing system can raise the scalability of the solution process. We also tried to fabricate an ink for solution process and optimized the printing system for high scalability. The detailed progress will be introduced in this chapter

2.2 synthesis of single-walled carbon nanotube ink in aqueous solution

Recently, Interests for carbon nanotube-based devices have increased continuously. [1]-[3] To meet the needs for the carbon nanotubes, commercially available ink based on have been widely used, and many research group have tried to fabricate well-dispersed carbon nanotube ink with high quality. [4],[5] It is well noted that carbon nanotube has surface properties of hydrophobic and do not disperse in the aqueous solution. To solve the technical issues, there are two methods for dispersion of carbon nanotube. One is the use of organic solvent, and the other is surfactant. The former is very simple method; the functionalized groups in the aromatic solvent depart the each carbon nanotube and disturb the agglomeration of the carbon nanotube resulted from the van der Waals force. [6] Although this is simple method, most organic solvents are toxic and noxious to human body. The latter is the use of addictive in the solution for dispersion stability. There are some surfactants having both hydrophilic and hydrophobic groups in the molecular structure. [7] The hydrophobic groups in the molecular structure attached on the carbon nanotube and the hydrophilic groups held the water molecule in the aqueous solution. The well-attached surfactants on the carbon nanotube improved the dispersion stability of the carbon nanotube in the aqueous solution. Commercially available aqueous inks also use the surfactant. But, they have other additives such as binder; information for the contents or the kind of the addictive is not given. So, there are additional problems resulted from the uninformed additive materials. Many research groups related with carbon nanotube have used synthesis of ink used only surfactant. [8]-[10] When we know the information of surfactant, we can choose the post treatment to reduce the surfactant. The groups have tried to optimize the contents and the kind of the additive are in the synthesized solution; the most famous surfactant for dispersion stability of carbon nanotube in the aqueous solution is sodium dodecylbenzene sulfonate (SDBS). [10] The surfactant has higher dispersion stability of carbon nanotube than other surfactant.

We also used the SDBS as surfactant enhancing dispersion stability of carbon nanotube in water. The optimized weight ratio between surfactant and carbon nanotube was reported as 10:1. But we considered a loss of carbon nanotube during filtration performed in the later, and set the weight ratio 10:1.5. At first, the carbon nanotube powder synthesized by arc−discharge method and water were mixed using tip sonication. When we used ultra−sonication for dispersion, the ink did not disperse well. The working and rest times of tip sonication during a period were set as 0.5 seconds. The working time was 20 minutes. The surfactant did not include in the first sonication, because each carbon nanotube is tangled in the powder. When the untangled powder and surfactant are mixed, the surfactant could not attach on the carbon nanotube surface effectively. To reduce this problem, carbon nanotubes in water solution except surfactant were dispersed using tip−sonication at first. [12] Then, the surfactant was added in the solution and the tip sonication was further performed for 20 minutes. An ultracentrifugation of the fabricated solution was performed at 5,000 RPM during 30 minutes to reduce untangled particle in the solution. After ultracentrifugation, only upper region in the resulted solution was collected using pipette. A filtration using filter paper is performed in the last process. The filtration is critical process for preventing agglomeration of carbon nanotube on the nozzle of the cartridge used for the inkjet printing system. [13] When much ink was filtered using one filter paper, the concentration of the ink decreased. So, we used one filter paper for filtering solution of 5 mL. The fabricated ink had higher dispersion stability than 6 months.

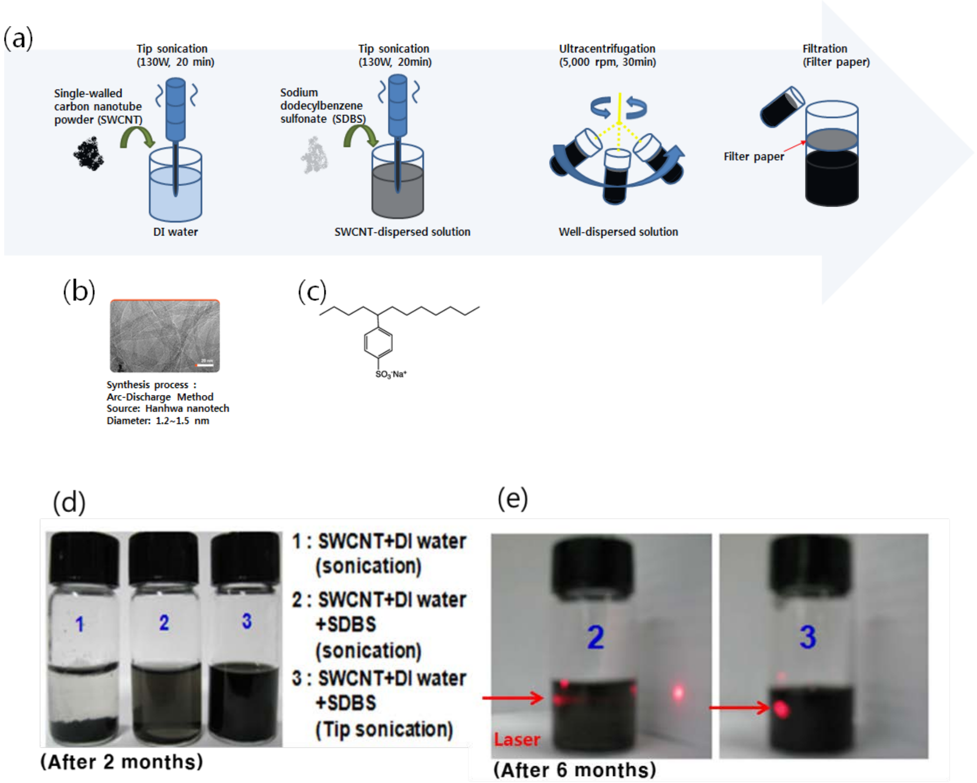


Fig. 2.1 Fabrication of single−walled carbon nanotube based ink. (a) Schematic flow of ink synthesizing process (b) Information of the single−walled carbon nanotube (c) Molecular structure of sodium dodecylbenzene sulfonate. Comparison of the effect of the tip sonication on the dispersion stability (a) after 2 months, (b) after 6 months

2.3 Printing conditions of the synthesized ink

We used inkjet printer made from Fujifilm dimatix inc., the operation principal of the printer is piezoelectric type. There are two types of the cartridge for the inkjet printer; the specification of the cartridge is determined by the volume of one ink drop. When ink in the cartridge goes through the nozzle of the cartridge, the volume of one ink drop is determined by the size of nozzle. The cartridge of 1 pL has 9 μm of nozzle size, and one ink drop jetted from the cartridge has about 1 pL of volume. While the cartridge of 10 pL has 21 μm of nozzle size, and it enlarge the size of one ink drop. The resulted films from the jetted ink are also affected by the size of ink drop. If a narrow line is needed, the small size of nozzle in the cartridge is essential. In some research areas for electronic devices, pemtoliter inkjet printer having a tiny size of nozzle is tested to meet the needs for narrow line or channel. [14] But, we used the cartridge having 21 μm of nozzle size in this experiments.

In order to fabricate well-shaped pattern using inkjet printer, some parameters should be optimized. Surface energy, temperature and drop spacing are important parameters, and they affect the shape of the printed pattern. When we used materials with different surface energy, the surface energy is critical issue for inkjet printing system. In this system, we used aqueous solution and poly(dimethlysiloxane) (PDMS) substrate; the materials have different surface energy. The water has hydrophilic surface properties, while the PDMS used for substrate has hydrophobic surface properties. When the water printed on the PDMS substrate, the contact angle between ink drop and substrate had high value as shown in fig 2.2; this means that the intended pattern do not have its shape. To reduce the hydrophobicity of the PDMS substrate, it was reported that the imported hydroxyl group during UV ozone treatment improve the quality of printed film. [15],[16] When the treatment was subjected to the PDMS substrate with a long time (> 60 min.), a thin layer of SiO_2 formed on the PDMS substrate. The UV ozone treatment should be optimized well because the formed SiO_2 is weak to the induced stress. Another solution to balance the different surface energy of two materials is surfactant. The surfactant has two types of functionalized groups; the groups reduce the gap of surface energy between the materials. [17] In our experiments, both methods were used for well-shaped pattern and film. The effect of each method could be confirmed by contact angles between PDMS substrate and ink drops. An ink drop on the PDMS substrate without surfactant and UV ozone treatment showed high contact angle. When the surfactant used for dispersion stability of carbon nanotube in aqueous solution was added, the contact angle has a drastic decrease. The contact angle had more reduction by the UV ozone treatment. When we compared the effect of the methods on the surface optimization for inkjet-printed aqueous solution by the contact angle, the surfactant in the solution was more effective than the UV ozone treatment.

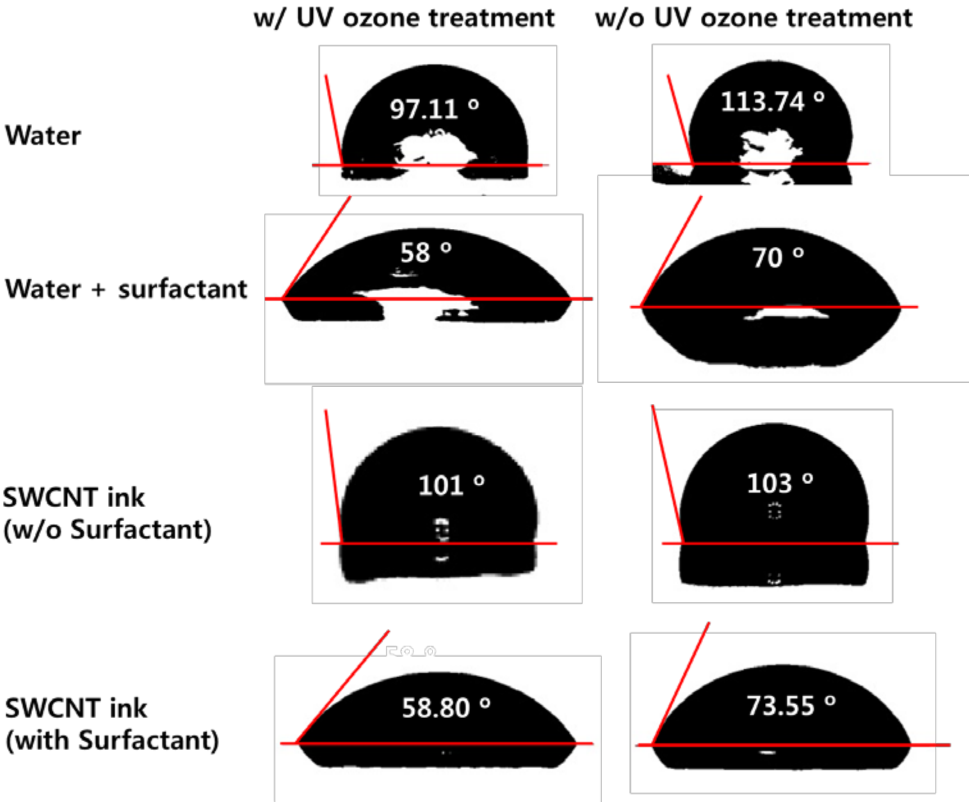


Fig. 2.2 Contact angles between solution drops and PDMS substrate with different treatments

The substrate temperature should be also considered for well-shaped films. Before the effect of substrate temperature on the film, we should check effect of surface tension. The printed aqueous solution exhibited some bead in the substrate than well-defined shape due to the effect of surface tension in fig 2.3. In case of multi-nozzle printing, the phenomenon was shown outstandingly, and it is hard to obtain clean edge of film. Although the UV ozone treatments reduced the phenomenon, the problem of low uniformity was not solved completely. To solve this problem, high substrate temperature was good solution in term of vaporization. Ii is well noted that the optimized substrate temperature is a critical option to form clean pattern line. [18] The effect of substrate temperature on the formed film was shown in fig 2.3. The formed film at high substrate temperature showed well-shaped film, while the printed results at low temperature showed circle shape rather than well-shaped film. A higher substrate temperature caused a nozzle clogging during the printing process. To prevent this nozzle clogging, we used 45 degree of substrate temperature.

When the printed ink drops were overlapped with a certain printing direction, the printed ink drops became a printed line. And, the continuous printing of the line get became the intended shape. The uniformity of the shape is determined by drop spacing which means distance between each ink drop. If the drop spacing is set as much shorter value than a diameter of one ink drop, the printed line has good edge properties and low surface properties. In contrast, longer distance between each ink drops than the diameter of one ink drop cause low edge properties in the printed line. To improve both film properties of edge and surface, the drop spacing had been used for a half of a diameter of one ink drop in the previous reports. [15] In our experiments, one ink drop on the UV ozone treated formed a circle with a diameter of 40 um, and we used the drop spacing of 20 um. In these conditions, the printed ink drop formed a printed line with good edge properties and the width of the printed line was 80 um. Although the edge property of the printed line is poor in the origin point of the inkjet printing, the edge properties improved in other positions.

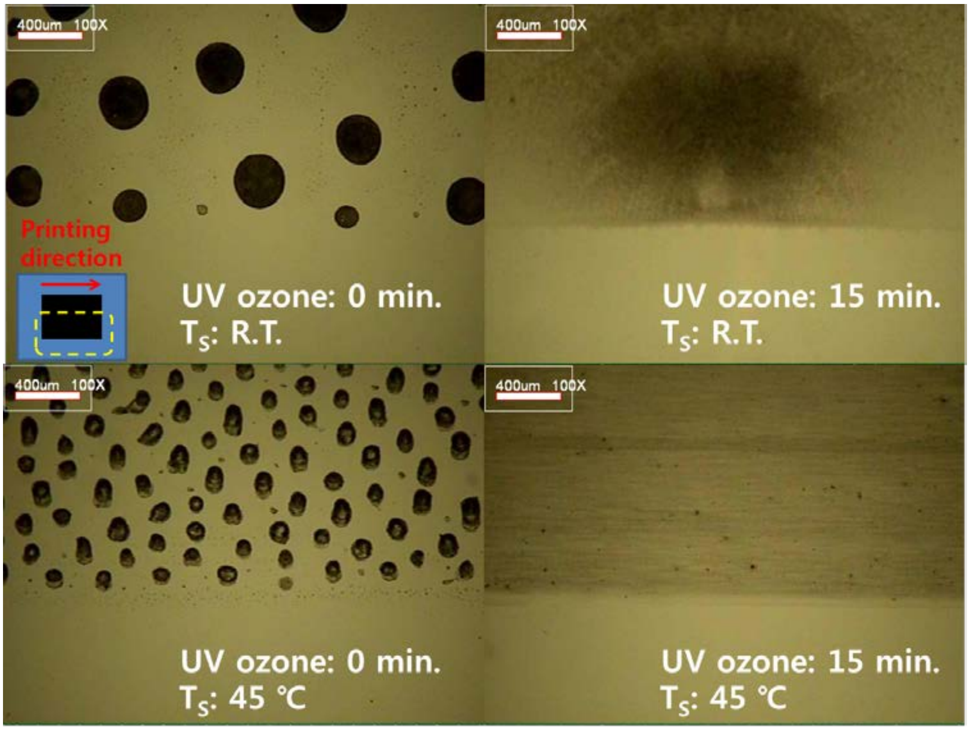


Fig. 2.3 Optical images of 1-layer printed SWCNT thin film on PDMS substrate with different conditions of substrate temperature (T_S) and UV ozone treatment

2.4 Fundamental properties of Inkjet-printed SWCNT film

The printed lines draw a certain shape using a printing pattern. Although the 1-layer printed thin film had conductivity and transparency, it is hard to use the thin film for stretchable electrode or strain sensor due to low conductivity and durability of the thin film under stressed situation. To obtain high properties for the use in the stretchable devices, several layers of SWCNT film were overlapped. When printing times increased, the conductivity of the printed thin film was improved and the transmittance decreased. A concentration of the single-walled carbon nanotube in the fabricated solution was 1.5 mg/mL, and it would be lowered during filtration. When we considered a weight fraction between carbon nanotube and water in the solution, the portion of carbon nanotube in the ink was low. So, the printed ink drop, line and film had transparency. The overlapped layer had higher density of carbon nanotube per unit area than 1-layer printed thin film; this cause the improved conductivity and lower transparency. But the multi-layered thin films still had low conductivity compared to the previous reports, [19]-[21] and many cracks occur in the film during mechanical deformation of the substrate. The pre-formed cracks were main sources which caused a drastic reduction of conductivity when external stress is subjected. To improve the mechanical properties of the printed thin film without the degradation, the film was washed using distilled water. In previous reports, the water rinsing is effective method for reducing the surfactant used for dispersion stability of carbon nanotube in the aqueous solution. [22],[23] In addition, we confirmed that the printed thin film could be easily wrinkled during bending. The pre-formed wrinkles in the thin film became the cracks during deformation mechanically; this caused a large reduction in conductivity of carbon nanotube thin film in the stretchable test. To prevent the wrinkle forming, the water rinsing was performed after inkjet printing of carbon nanotube ink on the stretchable substrate.

In addition, the washed film soaked into diluted nitric acid for improving the conductivity of the film. The post treatments to enhance the conductivity have been reported, and the nitric acid is well known as one of the p-type doping material for carbon materials. [24]-[26] When we performed diluted acid treatment (4 mol/L) on the washed thin film, we obtained a large reduction of sheet resistance of carbon nanotube as shown in figure 2.4.

After all process, thicknesses of the 1-, 2-, 3- and 5-layer printed film has 130, 140, 260, and 410 μm, respectively. The thickness was measured by alpha-step, and it was tried by several times to reduce measurement error. The thicknesses were measured in the perpendicular direction to the printing direction rather than the parallel direction having low edge properties. The thickness had a change during the post treatment as shown in figure 2.5. The change of the thickness and surface properties of the carbon nanotube thin film was exhibited to compare the effect of the post treatment. The surface properties of the printed thin film were confirmed by atomic force measurement. The results of the surface properties 5-layer printed film were shown in figure 2.6 respectively. After water rinsing, the thickness and surface properties changes. As-printed sample showed curved surface, while both sample performed by each treatment showed rough surface, even exhibiting shape of carbon nanotube. The surfactant, used as high weight fraction in the synthesized ink, was washed out, and this caused the changes of the thickness and surface properties. The results from the conductivity and the surface properties of the carbon nanotube film showed a reduction of the surfactant.

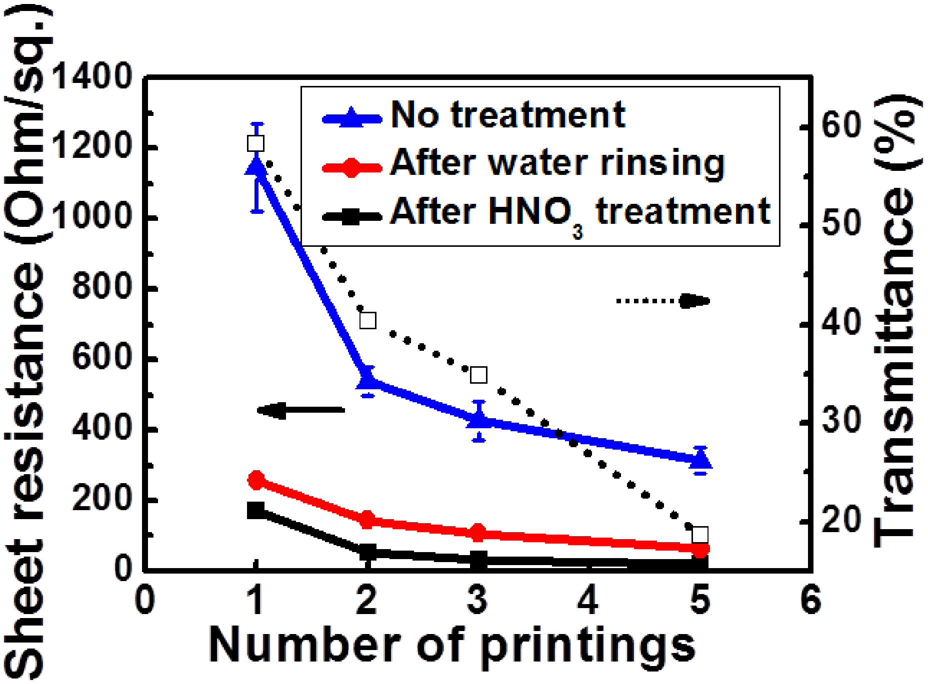
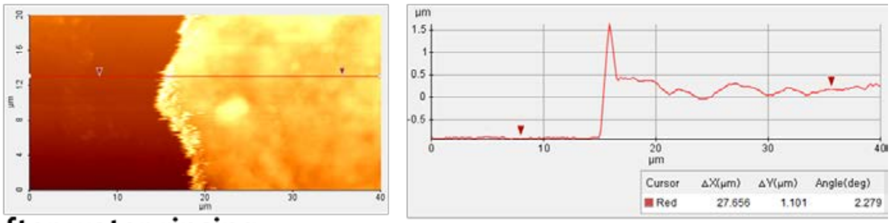
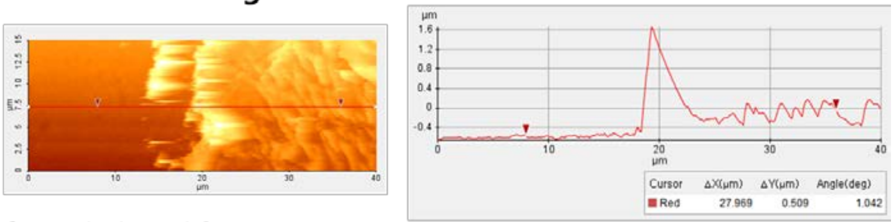


Fig. 2.4 Sheet resistance of 1-, 2-, 3-, and 5-layer printed SWCNT thin films that were untreated (closed triangle), rinsed (closed circle), and nitric acid-treated (closed square). Transmittance in the visible range (~380-780 nm) for each SWCNT thin film on a PDMS substrate, after all processes, is indicated by the open squares

(a) Before post treatments



(b) After water rinsing



(c) After nitric acid treatment

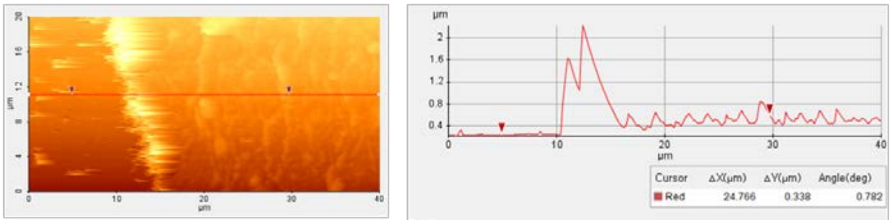


Fig. 2.5 Line profile value derivated from AFM results (left: AFM images, right: line profile value) of 5−layer printed SWCNT thin film (a) before post treatments (b) after water rinsing, and (c) after nitric acid treatment. To compare the thickness in the central region of the thin film, scotch tape detached some thin film located in the left side of the AFM image; this caused little delamination of the thin film

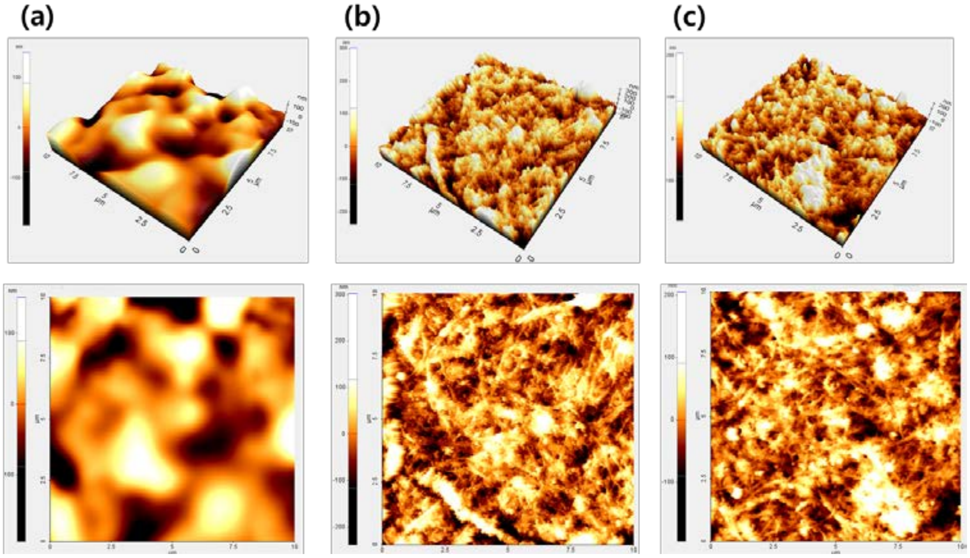


Fig. 2.6 AFM images of 5-layer inkjet-printed SWCNT thin film (a) before post treatments (b) after water rinsing, and (c) after nitric acid treatment

2.5 Conclusion

In summary, inkjet-printed single-walled carbon nanotube thin films on PDMS was obtained. To avoid the use of uninformed ink, we fabricated the ink using tip sonication, centrifugation, and filtration. The each conditions of the process were optimized, and the synthesized ink had good dispersion stability. Although water solvent in the aqueous ink did not spoil the PDMS substrate, a lot of optimized conditions of printing system were required because surface tension of water and the hydrophobic surface properties of the PDMS substrate. Surface tension of water resulting in circle shape of the printed film was solved using substrate temperature. The hydrophobic surface properties of the PDMS substrate caused high contact angle of printed ink and low edge properties of the printed film. UV ozone treatment on the PDMS and surfactant used in the fabrication process provided a large reduction of contact angle. However, the surfactant reduced the electrical properties of the printed film although the material had good effects for the properties of the dispersion and the contact angle. To reduce the surfactant and improve the electrical properties of the printed film, we tried the post treatments consists of water rinsing and diluted nitric acid; these treatment showed a significant effects on the properties of the electrical and surface

Reference

[1] S. Park, M. Vosguerichian, and Z. Bao, "A review of fabrication and applications of carbon nanotube film-based flexible electronics" Nanoscale, vol. 5, pp. 1727-1752, 2013

[2] P. Avouris and R. Martel, "Progress in Carbon Nanotube Electronics and Photonics" MRS BULLETIN, vol. 35, pp. 306-313, 2010

[3] C. Wang, K. Takei, T. Takahashi, and A. Javey, "Carbon nanotube electronics - moving forward" Chem. Soc. Rev., vol. 42, pp. 2592-2609, 2013

[4] http://www.nanointegris.com/

[5] http://www.hanwhananotech.com/

[6] J. Zhang, J. Yang, C. Yuan, G. Chen, and Y. Guo, "A convenient route to disperse pristine carbon nanotubes in polystyrene with no damage of nanotube electronic structure" J. Exp. Nanosci., vol. 8, pp. 573-578, 2013

[7] S. W. Kim, T. Kim, Y. S. Kim, H. S. Choi, H. J. Lim, S. J. Yang, and C. R. Park, "Surface modifications for the effective dispersion of carbon nanotubes in solvents and polymers" Carbon, vol. 50, pp.

3−33, 2012

[8] W. H. Duan, Q. Wang, and F. Collins, “Dispersion of carbon nanotubes with SDS surfactants: a study from a binding energy perspective” Chem. Sci, vol. 2, pp. 1407−1413 2011

[9] J. I. Paredes and M. Burghard, “Dispersion of Individual Single−Walled Carbon Nanotubes of High Length” Langmuir, vol. 20, pp. 5149−5152, 2004

[10] Z. Sun, V. Nicolosi, D. Rickard, S. D. Bergin, D. Aherne, and J. N. Coleman, “Quantitative Evaluation of Surfactant−stabilized Single−walled Carbon Nanotube: Dispersion Quality and Its Correlation with Zeta Potential” J. Phys. Chem. C, vol. 112, pp. 10692−10699, 2008

[11] M. F. Islam, E. Rojas, D. M. Bergey, A. T. Johnson, and A. G. Yodh, “High Weight Fraction Surfactant Solubilization of Single−Wall Carbon Nanotubes in Water” Nano Lett., vol. 3, pp. 269−273, 2003

[12] J. Hilding, E. A. Grulke, Z. G. Zhang, and F. Lockwood, “Dispersion of Carbon Nanotubes in Liquids” J. Dispersion Sci. Tech., vol. 24, pp. 1−41, 2003

[13] P. Beecher, P. Servati, A. Rozhin, A. Colli, V. Scardaci, S.

Pisana, T. Hasan, A. J. Flewitt, J. Robertson, and G. W. Hsieh, “Ink-jet printing of carbon nanotube thin film transistors” J. Appl. Phys., vol. 102, 043710 (7pp), 2007

[14] T. Sekitani, Y. Noguchi, H. Klauk, U. Zschieschang, and T. Someya, “Top-contact Organic Thin-Film Transistors Fabricated by Picoliter and Sub-Femtoliter Inkjets” ECS Trans., vol. 16, pp. 219-224, 2008

[15] S. Chung, J. Lee, H. Song, S. Kim, J. Jeong, and Y. Hong, “Inkjet-printed stretchable silver electrode on wave structured elastomeric substrate” Appl. Phys. Lett., vol. 98, pp. 153110 (3 pp), 2011

[16] H. Hillborg, N. Tomczak. A. Olah, H Schonherr, and G. J. Vancso, “Nanoscale Hydrophobic Recovery: A Chemical Force Microscopy Study of UV/Ozone-Treated Cross-Linked Poly(dimethylsiloxane)” Langmuir, vol. 20, pp. 785-794, 2004

[17] J. Seo and L. P. Lee, “Effects on wettability by surfactant accumulation/depletion in bulk polydimethylsiloxane (PDMS)” Sensors and Actuators B: Chemical, vol. 119, pp. 192-198, 2006

[18] D. Soltman and V. Subramanian, “Inkjet-Printed Line Morphologies and Temperature Control of the Coffee Ring Effect”

Langmuir, vol. 24, pp. 2224−2231, 2008

[19] D. J. Lipomi, M. Vosgueritchian, B. C. -K. Tee, S. L. Hellstrom, J. A. Lee, C. H. Fox, and Z. Bao, “Skin−like pressure and strain sensors based on transparent elastic films of carbon nanotubes”, Nat. Nanotechnol., vol. 6, pp. 788−792, 2011

[20] G. Gruner, “Carbon nanotube films for transparent and plastic electronics”, J. Mater. Chem., vol. 16, pp. 3533−3539, 2006

[21] Y. Zhou, L. Hu, and G. Gruner, “A method of printing carbon nanotube thin films” Appl. Phys. Lett., vol. 88, 123109 (3pp), 2006

[22] J. -M. Bonard, J. -P. Salvetat, T. Stockli, W. A. Heer, L. Forro, and A. Chatelain, “Field emission from single−wall carbon nanotube films” Appl. Phys. Lett., vol. 73, 918 (3pp), 1998

[23] M. Zhang, L. Su, and L. Mao, “Surfactant functionalization of carbon nanotubes (CNTs) for layer−by−layer assembling of CNT multi−layer films and fabrication of gold nanoparticle/CNT nanohybrid” Carbon, vol. 44, pp. 276−283, 2006

[24] B. B. Parekh, G. Fanchini, G. Eda, and M. Chhowalla, “Improved conductivity of transparent single−walled carbon nanotube thin films via stable postdeposition functionalization”

Appl. Phys. Lett., vol. 90, 121913 (3pp), 2007

[25] W. Zhou, J. Vavro, N. M. Nemes, F. Borondics, K. Kamaras, D. B. Tanner, J. E. Fischer, "Charge transfer and Fermi level shift in p−doped single−walled carbon nanotubes" Phys. Rev. B, vol. 71, 205423 (7pp), 2005

[26] H. −Z. Geng, K. K. Kim, K. P. So, Y. S. Lee, Y. Chang, and Y. H. Lee, "Effect of Acid Treatment on Carbon Nanotube−Based Flexible Transparent Conducting Films" J. Am. Chem. Soc., vol. 129, pp. 7758−7759, 2007

Chapter 3

Inkjet-Printed Stretchable Single-Walled Carbon Nanotube Electrodes with Excellent Mechanical Properties

3.1 Introduction

Recently, there has been intense research interest in the use of stretchable electronics for next-generation electronic device applications, for which device parts such as interconnects and driving circuits, and platforms must have good mechanical properties if they are to perform their functions under deformation.[1-3] Among these device components, stretchable interconnects have been most widely studied, but present the most significant research challenges. Although metals such as gold and silver have been studied for stretchable interconnects, they show poor mechanical properties, and plastic yielding under high strain.[4–6] Carbon nanotubes (CNTs) are therefore considered as a promising candidate for highly stretchable interconnects, owing to their excellent mechanical properties.[7] CNTs have been widely applied as stretchable electrodes for organic thin film transistors[7] and organic light emitting diodes,[8] as well as pressure[9] and strain sensors.[10] However, previous studies investigating stretchable interconnects were based on composite CNT/elastomeric matrix structures (which require the use of ionic liquids to achieve uniform dispersion),[7,12] the layering of CNT films between two polydimethylsiloxane (PDMS) substrates,[11] or an aerogel CNT backfilling process.[13] These processes are not suitable for the generation of large-area patterned electrodes, because of the complex and laborious processes that are required. A patterned CNT interconnect based on a screen printing method was reported to show a good conductivity of 102 S/cm, and good stretchability under 118% strain.[14] However, the screen printing method still requires the use of laborious processes for the synthesis of the CNT ink; in addition, ink is wasted during the patterning process, and different stencil shadow masks are required to create corresponding, different electrode patterns. Further, CNT-based electrodes typically show a higher initial resistance compared with their metal counterparts. Although CNT is a well-known material whose electrical properties can be controlled using doping methods, only a few studies have investigated CNT doping in stretchable electronics.[9,15]

Here, we describe the simple inkjet printing of single-walled carbon nanotube (SWCNT) stretchable electrodes, and their post-treatment processing. The inkjet-printing method holds many advantages over conventional methods in terms of its easy patterning nature, low fabrication costs, and large-area scalability. To reduce the initial resistance, post-treatments were performed. The relationship between the electrical and mechanical properties was confirmed by measuring the stretching of the SWCNT thin film. The SWCNT electrode was integrated with a light emitting diode to confirm the feasibility of its use for stretchable electronics applications.

3.2 Material and equipment for inkjet-printed single-walled carbon nanotube stretchable electrode

SWCNT thin films were prepared using an inkjet printer (Dimatix 2831, Fujifilm Dimatix Inc., Santa Clara, CA, USA) and an aqueous SWCNT ink. The aqueous ink was synthesized by applying tip sonication to an SWCNT (HANOS ASP-100F, Hanwha Nanotech, Seoul, South Korea) and sodium dodecylbenzenesulfonate (SDBS, Sigma Aldrich, St. Louis, Missouri, USA) mixture with a weight ratio of 3:20. The ink was then filtered using filter paper (NO. 541, Whatman, Maidstone, UK), to prevent the printer nozzle from clogging. PDMS substrates were fabricated by mixing PDMS (Sylgard 184, Dow Corning Corp., Midland, MI, USA) and its curing agent at a weight ratio of 10:1. Before the SWCNT ink was printed on the PDMS substrate, an ultraviolet (UV) ozone treatment was performed on the PDMS substrate for 10 minutes, to increase the wetting properties of the aqueous SWCNT ink; this was necessary because of the PDMS' s hydrophobic properties.[16] After the SWCNT ink was printed on the PDMS substrate, water and diluted nitric acid (4 mol/L) were sequentially drop-casted to reduce the amount of SDBS,[17] and to further improve the initial electrical properties of the SWCNT films, respectively. Each treatment step was performed for 1 hour. Previous papers have reported doping materials that increased the initial electrical properties.[18,19] Based on our experience with several acidic materials, the drop casting of diluted nitric acid was determined to be the simplest process, and the most compatible with the SWCNT thin film formed on the PDMS substrate.

Figure 3.1 (a) shows a schematic illustration of the processes used to fabricate the inkjet-printed SWCNT electrodes. When the cartridge temperature (40° C) and the ink drop velocity (~6-7 m/s) were optimized in the ink-jetting process, each ink drop on the UV ozone-treated PDMS formed a circle with a diameter of 40 μm. To form an electrode with a smooth surface and clean edges, we used ~1-2 cartridge nozzles (with a nozzle diameter of 21 μm), and a drop spacing of 21 μm. The PDMS substrate was placed on a heated (45° C) platen to prevent the agglomeration of ink drops; the resulting films had a line width of approximately 80 μm. A series of the printed lines were fabricated by optimizing the space between the lines. It was possible to obtain a minimum line spacing of approximately 25 μm, and both the line width and the spacing could be further reduced if smaller nozzles were used. Optical images of the fabricated thin films are shown in Fig. 3.1 (b). The SWCNT electrode had a dog−bone shape, with two square pads (0.5 × 0.5 cm^2) and one narrow line (0.1 × 3.0 cm^2). Both ends were fixed to a stretching apparatus using an adhesive (3145 silicone adhesive, Dow Corning), to allow uni−axial stretching tests to be performed. The inkjet−printed SWCNT thin films had intrinsically poor initial electrical properties, so the water rinsing and nitric acid treatments were sequentially applied to improve their electrical properties. The thickness, resistance, and transmittance were measured using an ALPHA−STEP instrument (Nanospec AFT/200, KLA−TENCOR, Milpitas, CA, USA), a 4−point probe, and UV−vis spectroscopy, respectively. After all treatments, the average thicknesses of the 1−, 2−, 3−, and 5−layer printed SWCNT that were 130, 140, 260, and 410 nm, respectively.

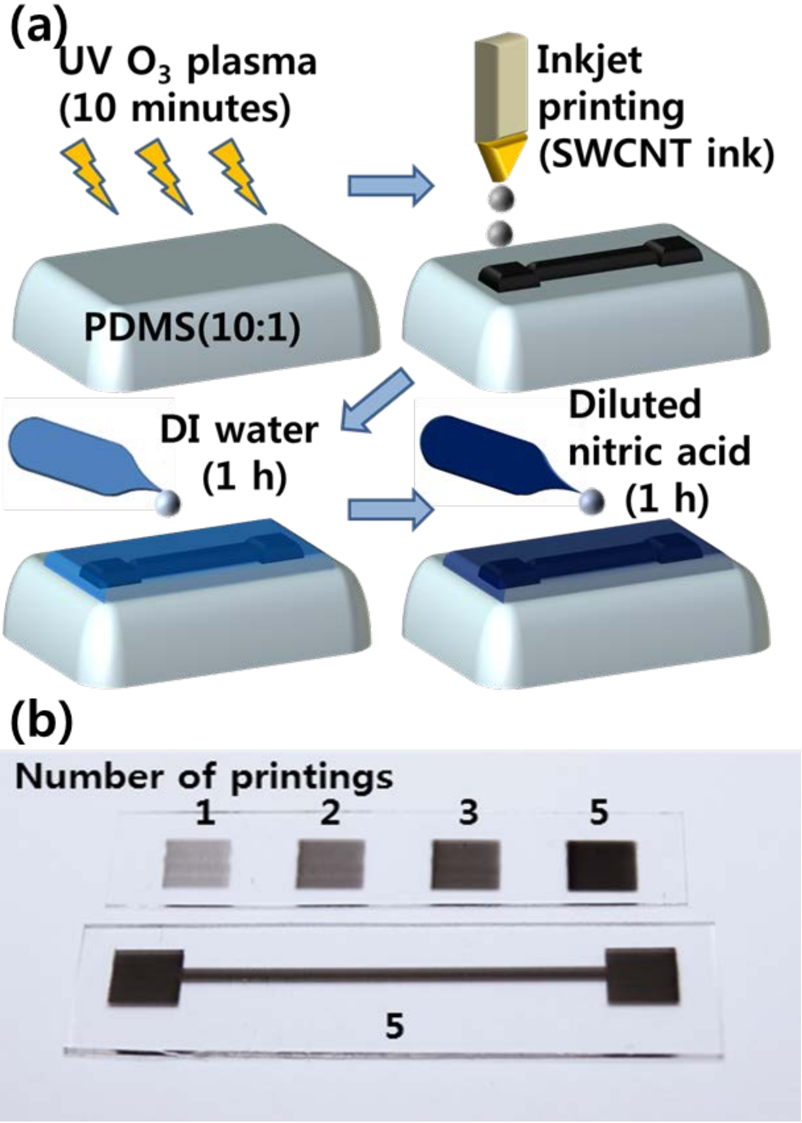


Fig. 3.1 (a) Schematic diagram of the process used to fabricate inkjet−printed SWCNT thin films on PDMS substrates using an aqueous SWCNT ink (b) Optical images of 1−,2−,3−, and 5−layer printed SWCNT thin films (square shape), and a 5−layer printed SWCNT thin film (dog−bone shape)

3.3 Excellent mechanical properties of inkjet-printed SWCNT thin film

Figure 3.2 shows the electrical properties of the inkjet-printed SWCNT thin films on the PDMS substrate, as measured during uni-axial stretching tests. To confirm the effects of the treatments on the SWCNT thin films, all of the samples were subjected to strains of up to 100%, using an extension speed of 1 mm/min; the results are shown in Fig. 3.2. Although all of the samples showed a slight increase in resistance under the tensile strain, the post-treatment processes greatly improved the performance of the electrodes. The surfactant used to increase the dispersion stability of the SWCNTs in aqueous solution caused a decrease in the electrical properties of the SWCNT thin films. In previous studies, SWCNT thin films were rinsed with water to reduce the amount of surfactant in the films, which were intended to have improved electrical properties.[17] In addition, some acid materials are p-type doping materials for CNTs.[20] We therefore applied water rinsing and acid treatments (sequentially) to increase the conductivity of the SWCNT electrodes. The treated SWCNT thin films showed a large reduction in their initial resistance and a large reduction in the variation of their resistance in the same strain range.

The electrical properties of the inkjet-printed SWCNT thin films on the PDMS substrate were measured during cyclic strain tests, for various printing times, as shown in Fig. 3.3 (a). The cyclic strain tests on the SWCNT thin films were performed using a strain of 50%, with a speed of 1 mm/min. All of the samples showed a sharp increase in resistance after the first stretching cycle, while after the second cycle the resistance variation showed oscillatory behavior. As the cycling number increased, the resistance showed saturation behavior, with small oscillations; this behavior was similar to that observed in previously reported investigations.[9,11,13] The variation in the resistance was minimal during the cycles subsequent to the first cycle—during which the conducting path was reduced—as long as the maximum strain was the same. This indicated that the SWCNT thin films could be used as high-performance stretchable electrodes after a single stretching cycle. Figure 3.4 (a) shows optical images of the cracks formed in the inkjet-printed SWCNT thin films after the first stretching cycle; the repeatable crack formation and de-formation processes that occurred during the subsequent cycles are also illustrated in this figure. Figure 3.4 (b) shows the SEM images that were taken at each stage, demonstrating the presence of the tangled SWCNTs that provided a good electrical connection under high tensile strain for the SWCNT films. Although cracks formed under the large strains that were applied, the tangled SWCNTs maintained their connections, even across large cracks, as shown in Fig. 3.4 (b); the connections between the SWCNTs prevented the cracks from propagating throughout the whole film, in contrast with inkjet-printed silver electrodes.[16] The formed cracks became increasingly narrower when the film was released, until a wrinkle structure was formed around them. This process was directly related to the oscillating behavior of the resistance after the second cycle, as shown in Fig. 3.3 (a).

To investigate the durability of the SWCNT thin films, we increased the cycling number, stretching speed, and strain range in the cyclic strain tests. Figure 3.3 (b) shows the resistances of 1- and 5-layer printed samples measured during a cyclic strain test with a high stretching speed (100 mm/min), and high strain (100%). The verisimilar oscillatory behavior was observed in the resistance of the printed samples even under such a harsh condition. The normalized resistance was determined as the ratio of the resistance measured after each cycle to the resistance measured after the first cycle; all of the thin films showed normalized resistances of less than 1.30, even at high cycling numbers. Although the films showed low normalized resistance values, the 5-layer printed film showed superior properties compared with the 1-layer printed film, in terms of its low initial and saturated resistances. Little variation in the resistance was observed during cyclic strain tests in previous studies of SWCNT stretchable electrodes.[11,13] However, most of these electrodes showed high initial resistances, or the tests were performed at low cycling numbers. Here, we obtained inkjet-printed SWCNT thin films that provided excellent electrical properties under high stretching speeds and high cycling numbers under the high tensile strains.

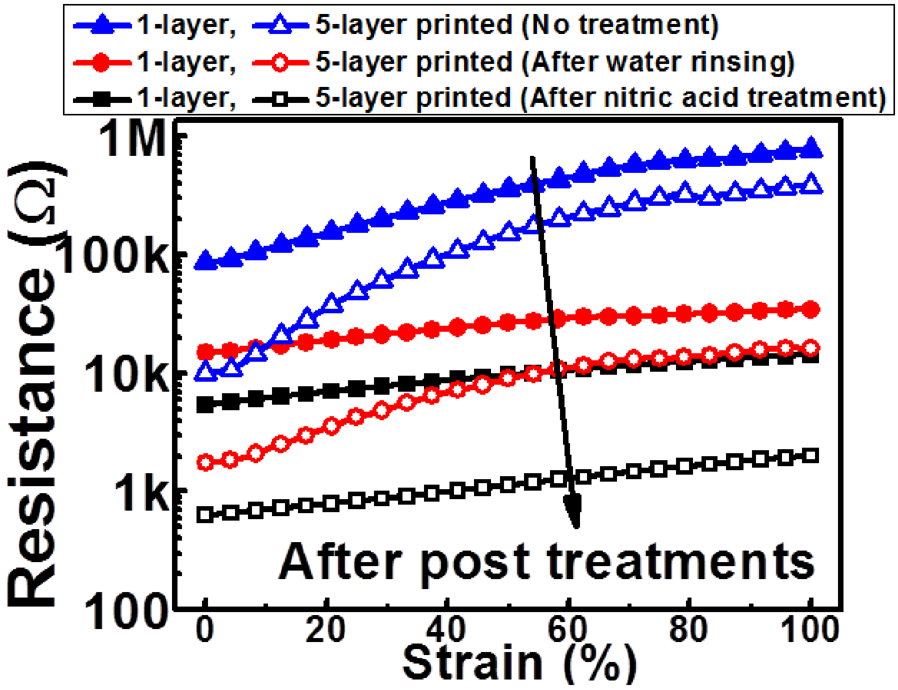


Fig. 3.2 Electrical properties of untreated (triangle), rinsed (circle), and nitric acid−treated (square) SWCNT thin films on PDMS substrate for strains up to 100%

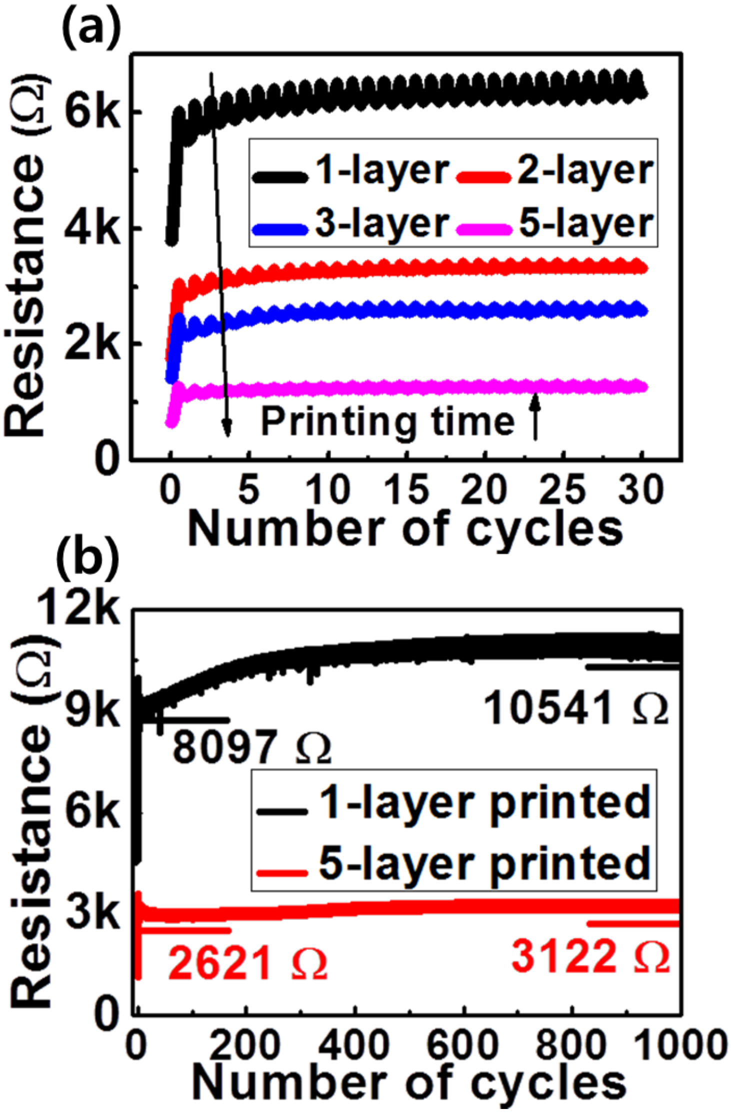


Fig. 3.3 (a) Electrical properties of SWCNT thin films (1−, 2−, 3−, and 5−layer printed samples) measured during cyclic strains tests for strains up to 50%, at a low speed (1 mm/min.) (b) Resistances of 1−and 5−layer printed thin films, measured during cyclic strain tests for strains up to 100%, with a high speed (100 mm/min.)

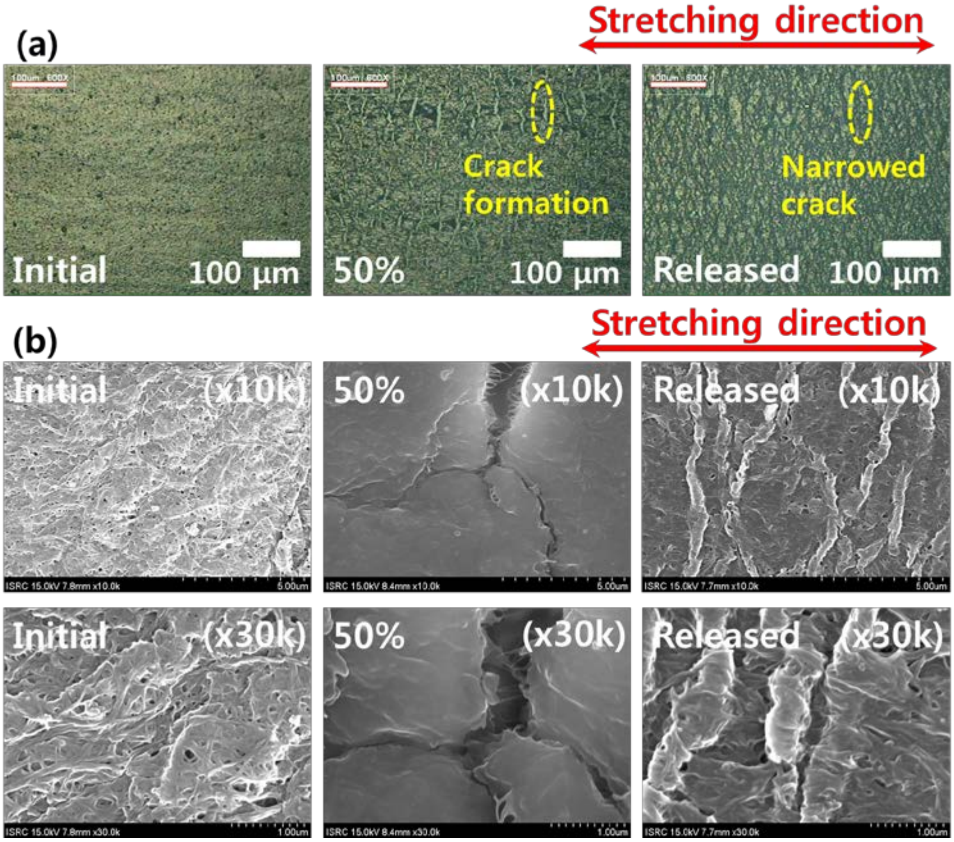


Fig. 3.4 (a) Optical images, and (b) SEM images of the SWCNT thin films (left: initial, middle: 50%-stretched, right: released state) during th strain tests

3.4 Applications of inkjet−printed SWCNT thin film

To investigate the potential usage of the inkjet−printed SWCNT thin films for stretchable electrode applications, the films were integrated with a light emitting diode (3 Φ blue LED, LEDJOY, Seoul, South Korea). The 5−layer printed sample was used in this stretchable lighting application test under a 500 mm/min stretching speed and 100% tensile strain. When the SWCNT thin film stretching cycle was performed, the LED showed good illumination, as shown in Fig. 3.5. The brightness was monitored using a chroma meter (CS−200, Konica Minolta Inc., Tokyo, Japan), which showed oscillating changes similar to the changes in the resistance shown in Fig. 3.3 (a) and (b). The relative brightness was reduced to 0.64 at 100% tensile strain, compared with the brightness at released state. Although there was some variation, a small variation in the resistance resulted in only a small variation in the brightness of the LED, even under 100% strain; these results indicated the potential of these SWCNT electrodes for highly stretchable electronic applications.

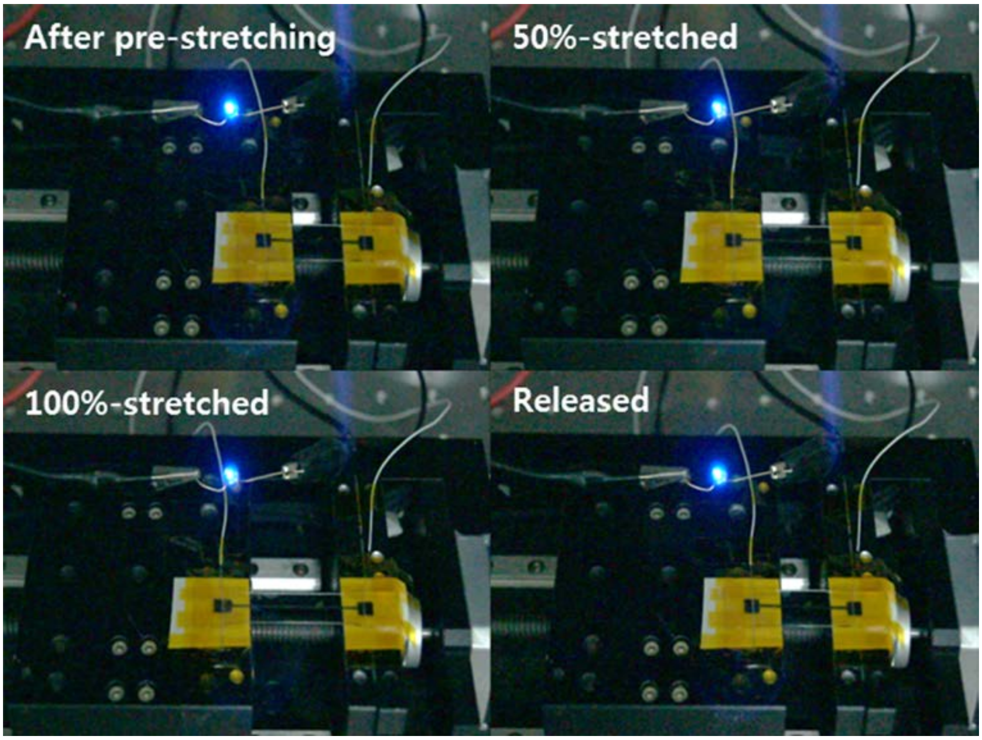


Fig. 3.5 Blue LED connected using a 5-layer printed SWCNT thin film, observed during cyclic strain test using a speed of 500 mm/min.

3.5 Conclusion

In summary, inkjet-printed SWCNT thin films on PDMS stretchable substrates were developed. Their initial electrical properties were improved via simple post-treatments that were compatible with the substrate. During cyclic strain tests, all of the thin films showed an irreversible increase in resistance during the first stretching, owing to the formation of cracks, as well as a very small, reversible variation during the rest of the cycles. These phenomena were confirmed under various fabrication and test conditions, by varying the number of layers printed, the stretching speed, and the strain. The 5-layer printed electrode showed small variations in the resistance under high strains and high stretching speeds. The 5-layer electrode was integrated with an LED and tested under high stretching speeds and high strains. The LED brightness was maintained during the cyclic strain tests, demonstrating these SWCNT-based electrodes as one of the best candidates for interconnection components in electronics applications where high stretching capabilities are required.

Reference

[1] J. A. Rogers, T. Someya, and Y. Huang, "Materials and Mechanics for Stretchable Electronics" Science, vol. 327, pp. 1603–1607, 2010

[2] T. Sekitani and T. Someya, "Stretchable, Large-area Organic Electronics" Adv.Mater., vol. 22, pp. 2228–2246, 2010

[3] T. Someya, T. Sekitani, S. Iba, Y. Kato, H. Kawaguchi, and T. Sakurai, "A large-area, flexible pressure sensor matrix with organic field-effect transistors for artificial skin applications" Proc. Natl. Acad. Sci. U. S. A., vol. 101, pp. 9966–9970, 2004

[4] J. Xiao, A. Carlson, Z. J. Liu, Y. Huang, H. Jiang, and J. A. Rogers, "Stretchable and compressible thin films of stiff materials on compliant wavy substrates" Appl. Phys. Lett., vol. 93, 013109 (3pp), 2008

[5] J. Jeong, S. Kim, J. Cho, D. Kim, and Y. Hong, "Stretchable Low Resistance Thick Silver Electrode on Poly(dimethlysiloxane) Compliant Elastomeric Substrate" Jpn. J. Appl. Phys., vol. 49, 05EB09 (4pp), 2010

[6] J. Lee, S. Chung, H. Song, S. Kim, and Y. Hong, "Lateral-

crack−free, buckled, inkjet−printed silver electrodes on highly pre−stretched elastomeric substrates” J. Phys. D: Appl. Phys., vol. 46, 105305 (5pp), 2013

[7] T. Sekitani, Y. Noguchi, K. Hata, T. Fukushima, T. Aida, and T. Someya, “A Rubberlike Stretchable Active Matrix Using Elastic Conductors” Science, vol. 321, pp. 1468−1472, 2008

[8] Z. Yu, X. Niu, Z. Liu, and Q. Pei, “Intrisically Stretchable Polymer Light−Emitting Devices Using Carbon Nanotube−Polymer Composite Electrodes” Adv.Mater., vol. 23, pp. 3989−3994, 2011

[9] D. J. Lipomi, M. Vosgueritchian, B. C−K. Tee, S. L. Hellstrom, J. A. Lee, C. H. Fox, and Z. Bao, “Skin−like pressure and strain sensors based on transparent elastic films of carbon nanotubes” Nat. Nanotechnol., vol. 6, pp. 788−792, 2011

[10] T. Yamada, Y. Hayamizu, Y. Yamamoto, Y. Yomogida, A. Izadi−Najafabadi, D. N. Futaba, and K. Hata, “A stretchable carbon nanotube strain sensor for human−motion detection” Nat. Nanotechnol., vol. 6, pp. 296−301, 2011

[11] Y. Zhang, C. J. Sheehan, J. Zhai, C. Zou, H. Luo, J. Xiong, Y. T. Zhu, and Q. X. Jia, “Polymer−Enbedded Carbon Nanotube Ribbons for Stretchable Conductors”, Adv. Mater., vol. 22, pp. 3027−3031,

2010

[12] S. Shang, W. Zeng, and X. Tao, “High stretchable MWNTs/polyurethane conductive nanocomposites” J. Mater. Chem., vol. 21, pp. 7274−7280, 2011

[13] K. H. Kim, M. Vural, and M. F. Islam, “Single−Walled Carbon Nanotube Aerogel−Based Elastic Conductors” Adv.Mater., vol. 23, pp. 2865−2869, 2011

[14] T. Sekitani, H. Nakajima, H. Maeda, T. Fukushima, T. Aida, K. Hata, and T. Someya, “Stretchable active-matrix organic light-emitting diode display using printable elastic conductors” Nat. Mater., vol. 8, pp. 494-499, 2009

[15] T. A. Kim, H. S. Kim, S. S. Lee, and M. Park, Single−walled carbon nanotube/silicone rubber composites for compliant electrodes” Carbon, vol. 50, pp. 444−449, 2012

[16] S. Chung, J. Lee, H. Song, S. Kim, J. Jeong, and Y. Hong, “inkjet−printed stretchable silver electrode on wave structured elastomeric substrate” Appl. Phys. Lett., vol. 98, 153110 (3pp), 2011.

[17] L. Hu, J. W. Choi, Y. Yang, S. Jeong, F. L. Mantia, L. F. Cui, and Y. Cui, “Highly conductive paper for energy−storage devices”

Proc. Natl. Acad. Sci. U. S. A., vol. 106, pp. 21490−21494, 2009

[18] H. Z. Geng, K. K. Kim, K. P. So, Y. S. Lee, Y. Chang, and Y. H. Lee, "Effect of Acid Treatment on Carbon Nanotube−Based Flexible Transparent Conducting Films" J. AM. Chem. Soc., Vol. 129, pp. 7758−7759, 2007

[19] B. B. Parekh, G. Fanchini, G. Eda, and M. Chhowalla, "Improved conductivity of transparent single−wall carbon nanotube thin films via stable postdeposition fuctionalization" Appl. Phys. Lett., vol. 90, 121913 (3pp), 2007

[20] W. Zhou, J. Vavro, N. M. Nemes, and J. E. Fischer, "Charge transfer and Fermi level shift in p−doped single−walled carbon nanotubes" Phys. Rev. B, vol. 71, 205423 (7pp), 2005

Chapter 4

A highly sensitive and repeatable strain sensor based on inkjet−printed single−walled carbon nanotube

4.1 Introduction

Advance developments in stretchable and flexible electronics device components have allowed various electronic devices to perform their function under tensile strain. [1]−[5] The developments in term of materials [6],[7], fabrication method [8], and system [9],[10] improve the properties of the electronic devices under deformation. For example, a metal has good conductivity and poor stretchability resulted from crack in microstructure; this disturbs the use of metal electrode in the stretchable electronics. [11] Some papers have tried to solve this problem of the metal−based stretchable electrode using structural approaches such as wavy or wrinkled structure of stretchable electrode. [12],[13] These systematic and comprehensive efforts lead to a drastic development in area of stretchable electronics application. A strain sensor measuring the length of the devices under deformation is one of the stretchable electronics applications that also require the endeavor to meet the demand in recent development

Strain sensor has been widely studied for detecting structural fracture in the building and bridge since the pieozoresitivity of silicon wire was observed under tensile strain. [14],[15] As other types of strain-dependent phenomenon such as tunneling effect of percolated conductive materials in non-conductive materials matrix have been applied to strain sensor application, the range of detectable deformation has been expanded [16],[65] ; this expansion provides the potential to the strain sensor in various stretchable electronic devices. The semiconducting based strain sensors using the band gap shift that depend on inter-atomic spacing under tensile strain have high gauge factor, defined by GF $= \frac{dR/R0}{dL/L0}$, as 120~150 in small tensile strain (<0.3%).[14],[17] The gauge factors of metal foil based strain sensor are about 2 because the Poisson's ratio of the metal is typically 0.25~0.35. The metal foil based strain sensor has reversible response to the tensile strain less than 2% due to a rapid change of microstructure ratio when plastic deformation in the metal occurred.[18] Conductive fillers in textile or composite based strain sensor have conducting path; the conducting paths are de-constructed under deformation. Although the polymer composite based strain sensors detect large deformation, the response of the strain sensors on the applied strain is not proportional to the changes in length. [19],[20]。

Figure 4.1 and table 4.1 introduce the conventional products for measuring the strain, and various strain sensor reported recently are introduced in term of sensitivity and strain range. It is noted that fracture of fiber in the skin take place at the strain range higher than 25% and the skin stretch on the back of the hand caused by flexion movement of index finger is higher than 3~6%. [21]-[23] But, most previous studies for semiconducting and metal gauge are not suitable due to low strain range. [17],[48],[49] Composite based strain sensors that reported high strain range could detect the tensile strain of skin, but they showed non-linear response on the change in length. [54] High sensitive and stretchable strain sensor is essential to meet the demand for wearable electronic devices such as smart glove, health monitoring system, and electronic skin. Recent studies for strain sensor device are focused on the single-walled carbon nanotube (SWCNT) thin films that are formed by spin coating or transfer method; these strain sensor also undergo low gauge factor. [24],[34],[40] High mechanical properties of material and the systematic efforts to reduce the disadvantage of the materials are challenging for further development in the strain sensor device.

Here, we introduce a new concept of strain sensor based on inkjet-printed SWCNT thin film on stretchable substrate using periodically ordered cracks in the thin film. The strain sensor shows high gauge factor and good durability in high strain range. The inkjet-printed SWCNT thin film has good durability and high sensitivity resulted from the periodically ordered cracks. There are various sensing properties of strain sensor such as linearity, stretching speed effect to measure human motion; these properties of the strain sensor show good performances. The stain sensor with excellent sensing properties can measure human motion from small vibration in back on the hand to ligament flexion.

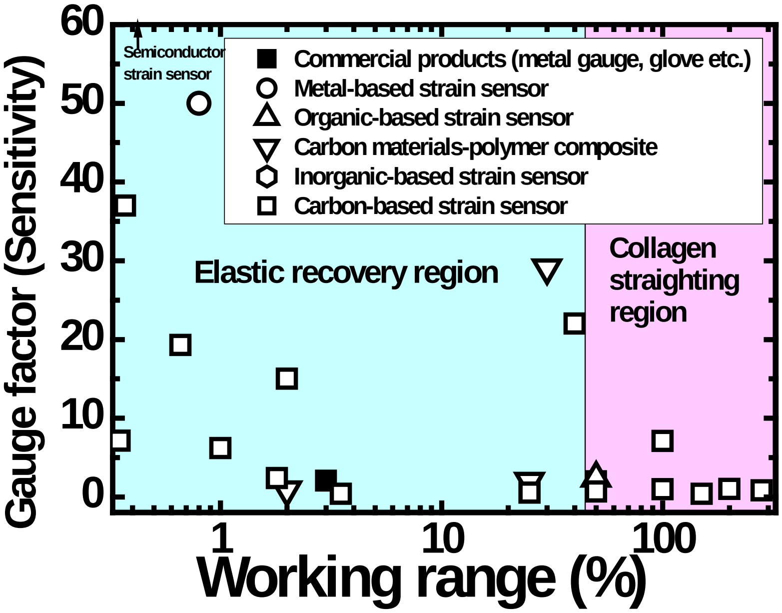
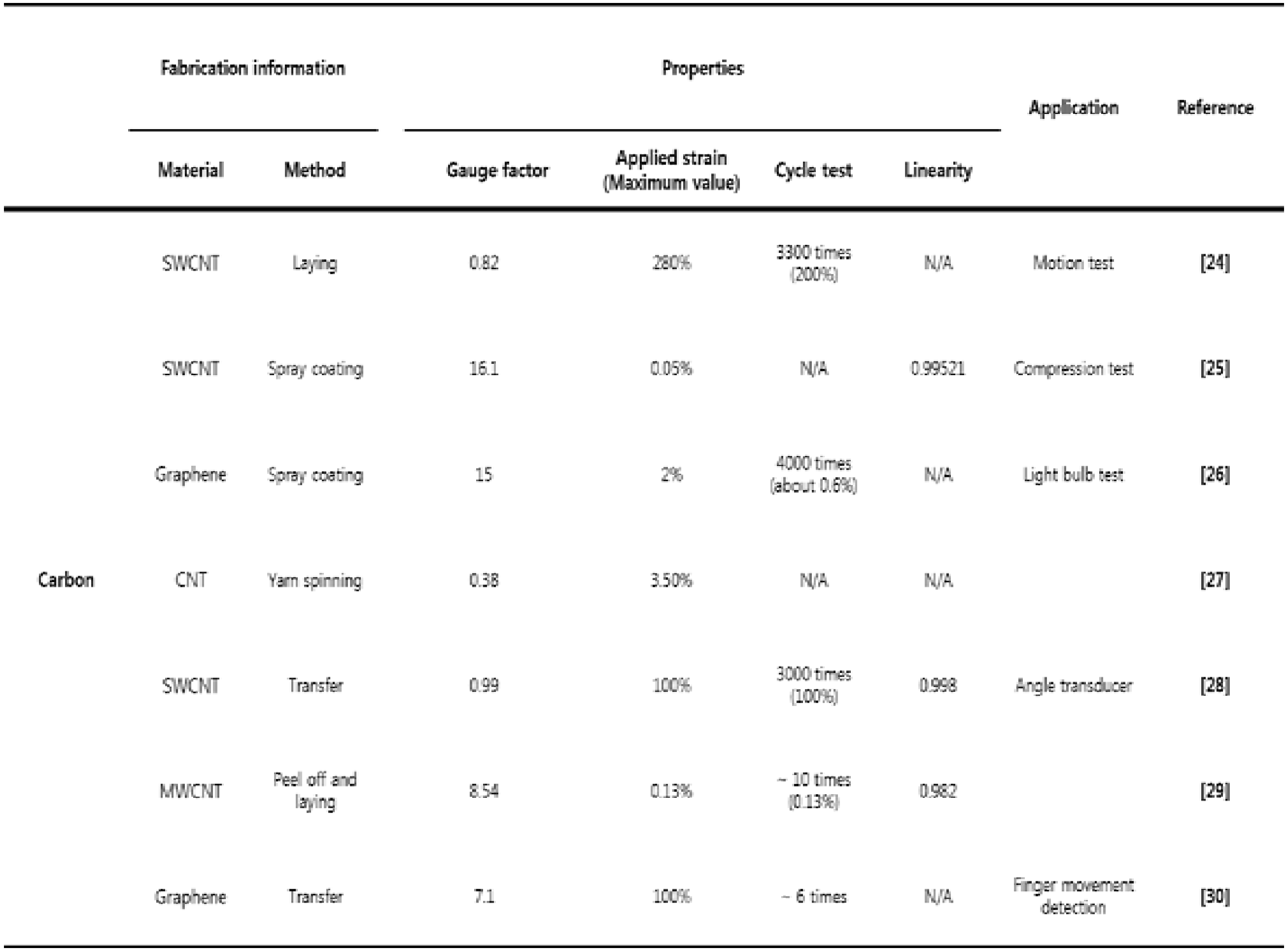


Fig. 4.1 Recent reports and commercial products for strain sensor plotted as function of gauge factor and working range. Human skin lose their elastic properties in the tensile stain up to 45~55% [22]



	Fabrication information		Properties				Application	Reference
	Material	Method	Gauge factor	Applied strain (Maximum value)	Cycle test	Linearity		
Carbon	SWCNT	Laying	0.82	280%	3300 times (200%)	N/A	Motion test	**[24]**
	SWCNT	Spray coating	16.1	0.05%	N/A	0.99521	Compression test	**[25]**
	Graphene	Spray coating	15	2%	4000 times (about 0.6%)	N/A	Light bulb test	**[26]**
	CNT	Yarn spinning	0.38	3.50%	N/A	N/A		**[27]**
	SWCNT	Transfer	0.99	100%	3000 times (100%)	0.998	Angle transducer	**[28]**
	MWCNT	Peel off and laying	8.54	0.13%	~ 10 times (0.13%)	0.982		**[29]**
	Graphene	Transfer	7.1	100%	~ 6 times	N/A	Finger movement detection	**[30]**

Table 4.1 Recent reports for strain sensor exhibited by fabrication information, properties, and applications [24]–[57]

	Fabrication information		Properties				Application	Reference
	Material	Method	Gauge factor	Applied strain (Maximum value)	Cycle test	Linearity		
Carbon	Graphene	Transfer	0.55	25%	N/A	N/A		**[31]**
	RGO	Syringe pump	7.14	0.35%	10000 times (0.35%)	N/A	Bending test	**[32]**
	Graphene	Stamping	2.4	1.80%	4 times (<1.8 %)	N/A	Glove test	**[33]**
	CNT	Transfer	1	200%	9000 times (100%)	0.9999	Glove, chest, balloon test	**[34]**
	Graphene woven fabrics	Transfer	>500	8%	100 times (8%)	N/A	Compression, torsion, shearing test	**[35]**
	Graphene	Transfer	150	0.08%	N/A	N/A		**[36]**
	SWCNT	Transfer	269	0.02%	10 times (0.004%)	0.996		**[37]**

	Fabrication information		Properties				Application	Reference
	Material	Method	Gauge factor	Applied strain (Maximum value)	Cycle test	Linearity		
Carbon	SWCNT	Spray coating +embedding	0.68	50%	N/A	N/A	Touch panel	**[38]**
	Nanographene	Growth on a s ubstrate	37 (tunable)	0.37%	4 times (<0.37 %)	N/A		**[39]**
	SWCNT	Spray coating	0.41(capacitive type) 0.19(resistive type)	150%	12500 times (25%)	0.969	pressure sensor	**[40]**
	Graphene nanoplatelet +MWCNT	Screen printing	2~22 (high filler concenstration), 100 (low filler concentration)	40%	7 times (40%)	0.93~0.99		**[41]**
	Graphene	Transfer	6.21	1.00%	4 times (1%)	N/A		**[42]**
	SWCNT +graphite nanoplatelet	Spray coating	5.01 (tunable)	0.16%	10000 times (0.1%)	N/A	Finger test	**[43]**
	SWCNT	Spray coating	59.2	0.04%	N/A	0.99521	Tension and compression test	**[44]**

	Fabrication information		Properties				Application	Reference
	Material	Method	Gauge factor	Applied strain (Maximum value)	Cycle test	Linearity		
Carbon	Graphite	Screen printing	19.3	0.66%	100,000 times (0.66%)	N/A		**[45]**
Organic	Polypyrrole -polyurethane	composite	2.4	50%	30 times	N/A		**[46]**
	PEDOT:PSS	Electrochemical polymerization	17.8	60 degree	6 times (60 degree)	N/A	Bending test	**[47]**
Metal	Gold nanoparticle	convective self-assembly	50	0.80%	12 times (0.3%)	N/A	Compression-tension test	**[48]**
	Silver nanoparticle	inkjet-printing	21	0.02%	N/A	N/A		**[49]**
Inorganic	ZnO-polystyrene	electrospinning	116	50%	<20 times (30%)	N/A	Integrated with solar cell	**[50]**
	Sb doped ZnO	CVD	350	0.20%	N/A	N/A	Writing test	**[51]**

	Fabrication information		Properties				Application	Reference
	Material	**Method**	**Gauge factor**	**Applied strain (Maximum value)**	**Cycle test**	**Linearity**		
Composite (Carbon material base)	RGO-PVDF	Composite	12.1	0.13%	< 5 times (0.13%)	N/A		**[52]**
	Graphene ribbon-PMMA	Transfer	2	25%	N/A	N/A		**[53]**
	Carbonblack-PDMS	Casting	29.1	30%	5 times (30%)	N/A		**[54]**
	SWCNT-PVDF	Compoiste	6.2	0.26%	160 times (0.26%)	0.99		**[55]**
	ZnO-cellulose composite paper	Sol-gel method	21.12	0.10%	5 times (0.06%)	N/A		**[56]**
	Polycarbonate-MWCNT or graphene nanoplatelet	Composite	0.92	2%	3 times (2%)	0.989		**[57]**

4.2 Effect of periodically-ordered patterns on the structural and electrical properties of the inkjet-printed SWCNT thin films

Figure 4.2 illustrates schematic flow of the fabrication and structure of inkjet-printed SWCNT based strain sensor. The synthesized SWCNT aqueous ink was printed with specific pattern or shape using an inkjet printer (Dimatix 2831, Fujifilm Dimatix Inc., Santa Clara, CA, USA). Poly(dimethlysiloxane) (PDMS) (Sylgard 184, Dow Corning Corp., Midland, MI, USA) substrate with inkjet-printed SWCNT pattern was subjected to UV ozone treatment to improve wetting properties of the PDMS substrate for 10 minutes. [13] 5-layer printed SWCNT thin film was printed on the UV ozone treated sample. To reduce surfactant used for the dispersion stability of SWCNT powder in aqueous solution, [58],[59],[60] a rinsing method using a pipette was performed on the SWCNT strain sensor for 1 hour, and then it was dried. Figure 1(b) shows the structure of the inkjet-printed SWCNT strain sensor on the PDMS substrate. Although the fabrication process is similar to the inkjet-printed SWCNT stretchable line introduced in previous chapter, there is a different step with the process of the stretchable line.

The Inkjet-printed SWCNT pattern exists between the inkjet-printed line and the PDMS substrate.

The effect of the printed pattern on the structural properties of the printed thin film is shown in the figure 4.3. As mentioned in the chapter, the printed thin film did not have cracks in the film if an external stress is not subjected. When applied stress (or strain) was subjected to the thin film, many cracks in the thin film initiated. The formed cracks propagated according to the magnification of the external stress. [24] Unlike the SWCNT thin film without pre-printed pattern, there were two types of crack in the SWCNT thin film with the pattern. Small crack took place randomly in the line and the crack did not propagate in whole thin film under low tensile strain due to fiber bridging behind crack tip. [61]-[63] Large scale crack near the printed pattern, even obviously observed in tensile strain of low magnification, propagated along the pattern under tensile strain. The opened cracks of both types became narrow and wrinkle structure when the external tensile strain was eliminated. The phenomenon of the repeatable crack formation in the SWCNT thin film could be observed in various pattern shapes such as circle and vertical line; this means that we can arrange the crack formed by the pre−printed pattern. As shown in the figure, the intended crack formed near the pre−printed pattern grew to the perpendicular direction of the external strain. If we consider that the crack formed under tensile stress disturb electrical current flow in the film, the vertical line is more effective shape for highly sensitive strain sensor.

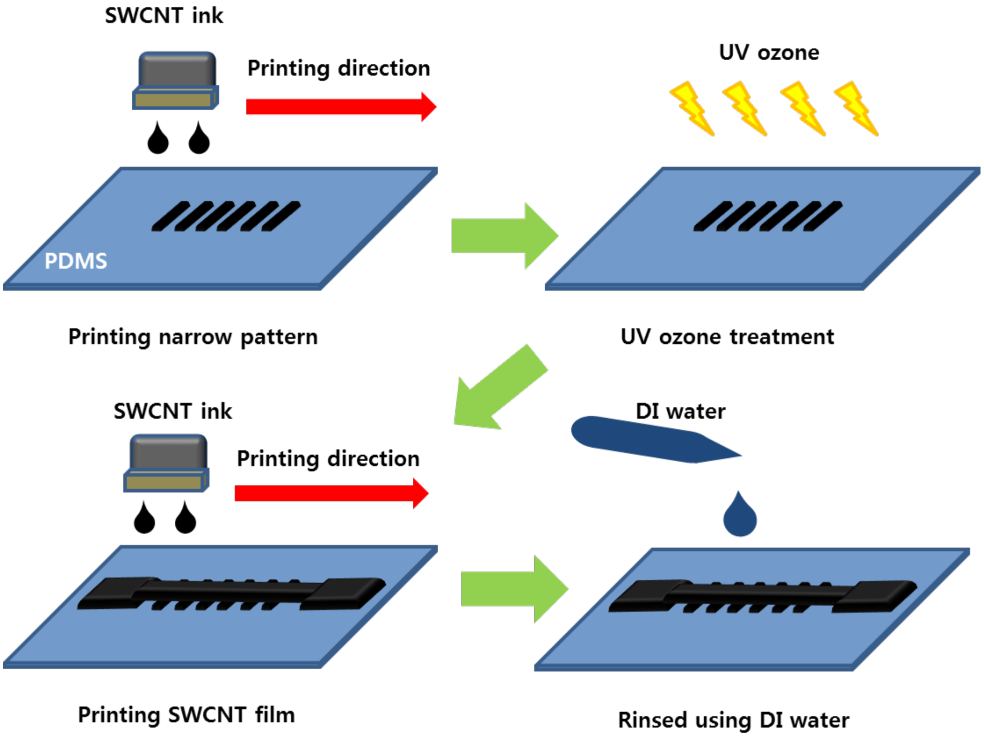


Fig. 4.2 Schematic diagram of the process used to fabricate inkjet-printed SWCNT strain sensor on PDMS substrates using an aqueous SWCNT ink

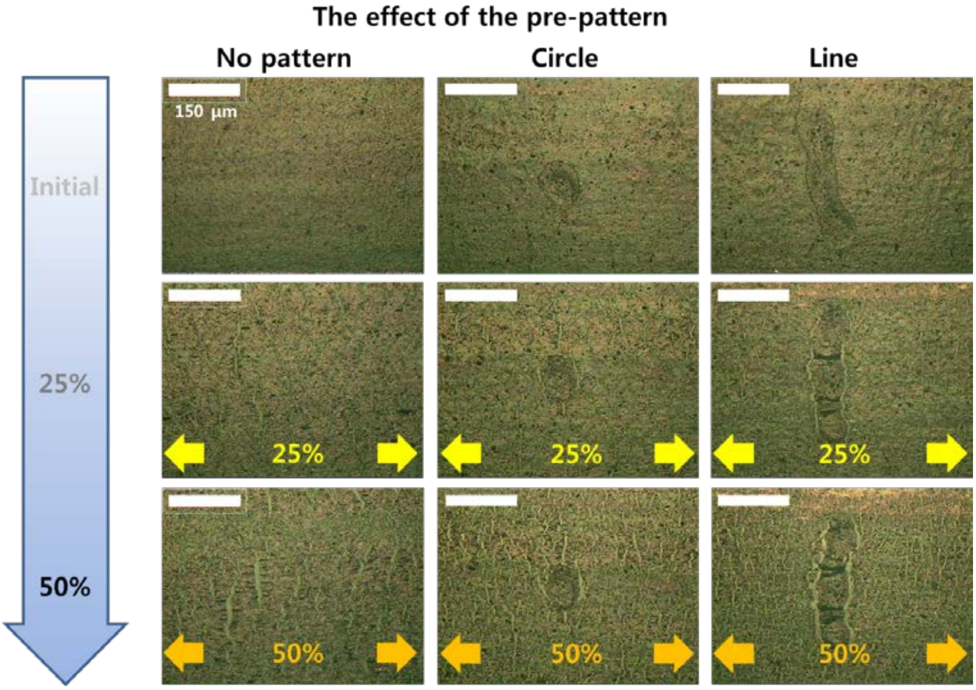


Fig. 4.3 Optical images exhibiting the effect of the pre−pattern on the structure of the 5−layer printed SWCNT thin films on the PDMS substrate for strain up to 25% and 50%, respectively (Shape of the pattern − left: without pattern, middle: circle, right: vertical line)

To further investigate the effect of the pre−printed pattern on the electrical properties of the printed SWCNT line, we optimized the shape and densification of the pre−printed pattern as shown in figure 4.4. The shape of the printed line was a dog−bone shape having two rectangular pads used for measuring the electrical properties of the thin film and a narrow line. The printed patterns located in the narrow line. The sensitivity of the printed strain sensor was determined by the shape of the pre−printed pattern resulting in ordered cracks. We fixed some conditions of the pattern such as width of the narrow line and length of the strain sensor and changed the density of the pre−printed pattern in length of the strain sensor and the size of the pre−printed patterns in the narrow line. The SWCNT stretchable line introduced in previous chapter had excellent mechanical properties under harsh conditions due to cracks formed randomly; the crack did not propagated to the whole thin film. However the cracks formed by the pre−printed pattern propagated to the whole thin film as shown in figure 4.4 (b) and (c), which cause a drastic reduction of the current path in the thin film. Periodic ordered patterns formed periodic and fully−propagated crack, the crack thin down the current path in the thin film effectively. Although the low scale cracks were exhibited in the thin film by the tensile strain, large scale crack cut off the thin film during stretching cycle; the effect of the large crack is dominant in the resistance of the thin film. All the cracks were de-formed at released state. The narrowed conducting path formed by ordered pattern is key issue for high sensitive strain sensor. The effects of the pre-pattern size and the pattern density on the sensitivity of strain sensor are observed as shown in figure 4.4 (d) and (e). Strain sensors with no conducting path (w: 0 mm) show high sensitivity to the tensile strain, but they had high sample variations due to the large scale crack formed in whole thin film. The conducting path with small scale crack prevents the resistance of the thin film from increasing unpredictably. When the ratio of conducting path in the printed line increased, a gauge factor of the strain sensor became 0.91; this is a comparable value with previously reported paper for thin film based strain sensor. [24],[38],[40] The periodically ordered and dense crack with narrow conducting path is most effective method for high sensitive strain sensor and the inkjet printer is well matched with high sensitive strain sensor in term of easy patterning and scalability.

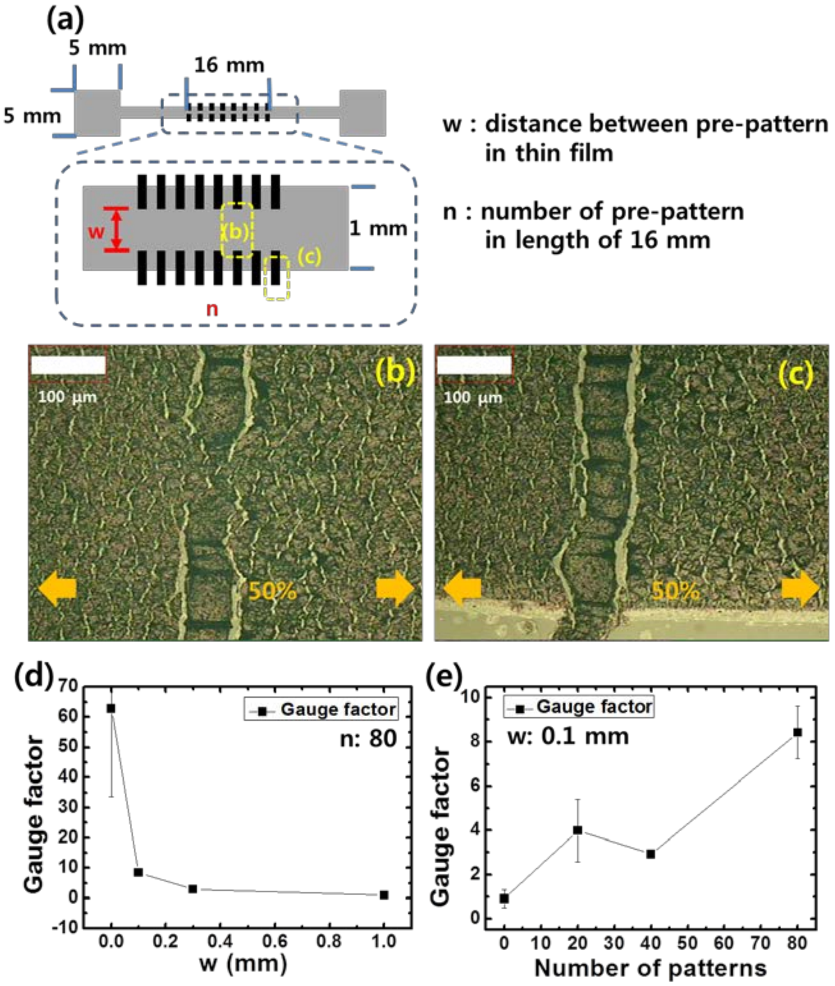


Fig. 4.4 (a) schematic illustration of inkjet-printed SWCNT strain sensor with pre-pattern having two variable conditions that are vertical distance between patterns and numbers of pattern in thin film. Optical images of the strain sensor for strain up to 50% (b) in central region and (c) in edge region of the thin film. Gauge factor variation controlled by the conditions of (c) the distance and (d) the number of pattern

The effect of the intended crack resulted from pre-printed pattern are observed in figure 4.5. The strain-sensitivity of the printed film changed when some treatments were subjected. To compare the changes, we prepared three types of 5-layrer printed thin film having different treatments each other and measured the resistance behavior of all samples during stretching cycle test. All samples were tested by strain increasing test for stains up to 12.5%, 25.0%, 37.5% and 50.0% respectively and the cycle were performed twice. The resistivities of the printed thin films at release state were continuously increased as the tensile strain increase; this is correlated with increasing crack density and size as shown in fig 4.3. This has been widely reported in the SWCNT or nanomaterial-based thin film due to crack or buckled structure. [34],[35],[40] In second stretching cycle, the resistances of the printed thin films at release state did not change significantly because the cracks did not propagate at the same maximum strain although the recovery of the resistivity in release state was late. As mention in the chapter 3, diluted nitric acid (4 mol/L) treatment performed on the washed SWCNT thin film reduced the resistivity of the thin film and resistance variation during the stretching test. In contrast to the acid−treated sample, the printed thin film having pre−printed pattern exhibited the high sensitivity on the applied strain. Unlike other types of the printed thin film having only randomly−formed crack, the printed thin film having the pre−printed pattern had two types of crack. The intended crack resulted from pre−printed pattern improved the sensitivity of the thin film on the applied strain by a limitation of current path; the strain−sensitivity of the thin film was higher than that of the thin film without the pre−printed pattern. We can confirm the intended crack is high effective method to improve the sensitivity of the stain sensor

So, we measured various specificities of the strain sensor as well as the sensitivity of the strain sensor to confirm the feasibility of the strain sensor.

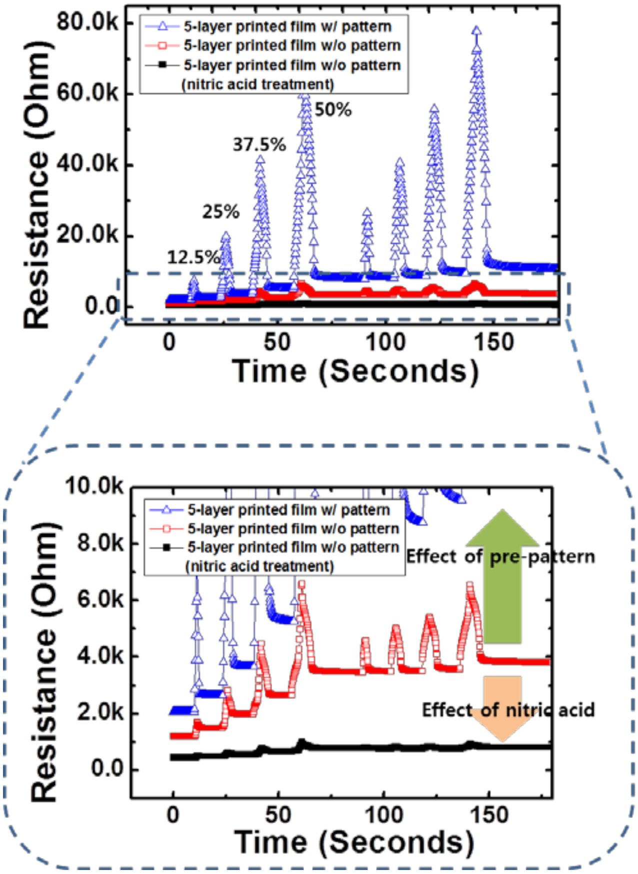
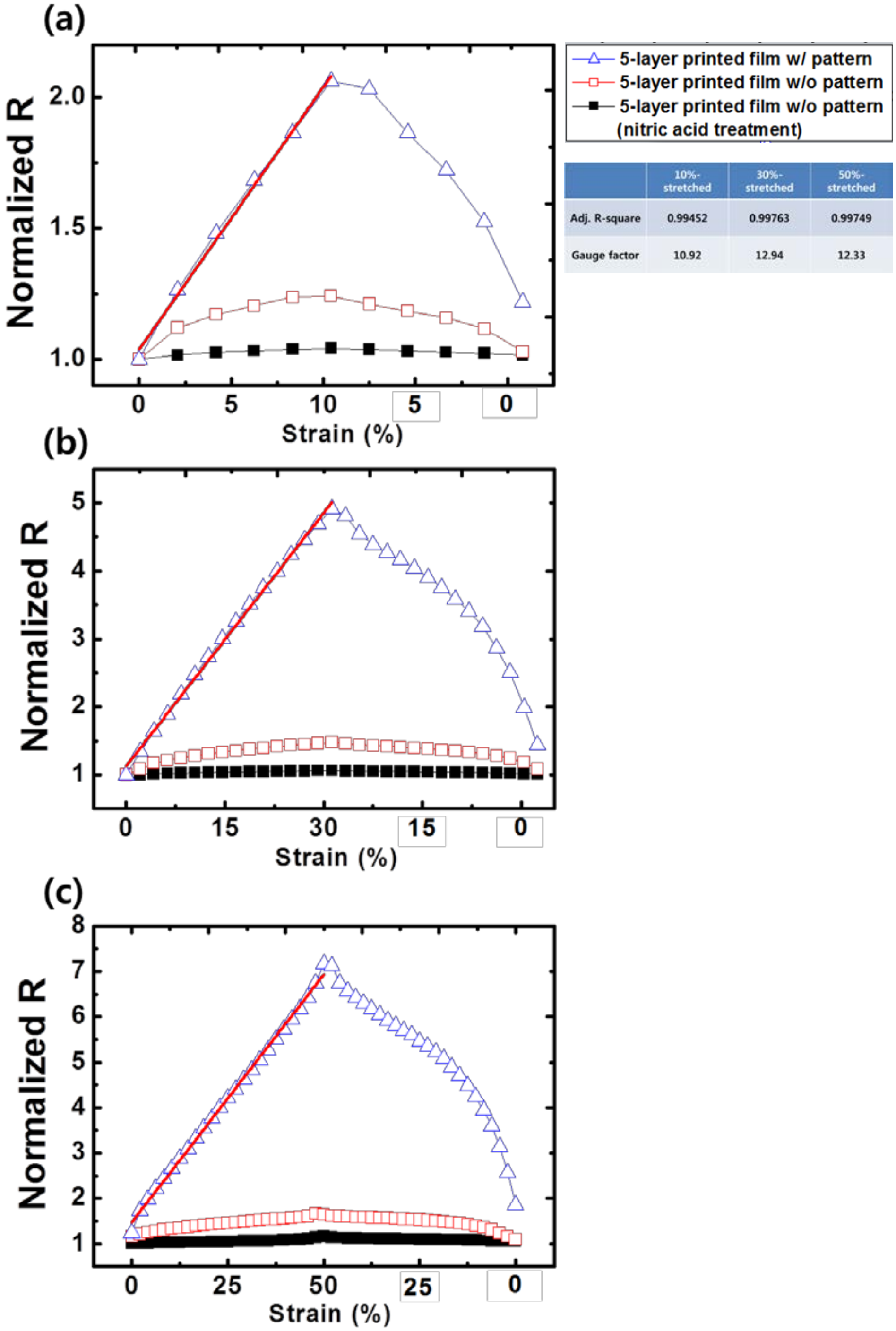


Fig. 4.5 Resistance variations showing the effect of the pre−pattern on the electrical properties of 5−layer printed SWCNT thin film having pre−pattern (w: 0.1 mm, n: 80) (open triangle) on PDMS substrate for strain up to 12.5, 25%, 37.5%, and 50% respectively and comparison results of 5−layer printed SWCNT thin film having no pattern (w: 0 mm, n: 0, rinsed sample−opened square, nitric acid treated sample−closed square) The stretching tests were performed twice.

4.3 Fundamental properties of the inkjet−printed strain sensor

Figure 4.5, 4.6, and 4.7 demonstrate properties of the strain sensor under uni−axial tensile strain test. The 5−layer printed lines optimized by pre−printed pattern are tested and the printed line was pre−stretched for strain up 50%. When the 5−layer printed strain sensor was subjected to the strain up to 10%, 30%, and 50% respectively, the variation of normalized resistance showed similar behavior under the tensile stress. Compared with the 5−layer printed thin film without pre−printed pattern, the strain sensor showed excellent sensitivity on the tensile strain in the whole range. They showed about 12 of gauge factor and it had little change in various strain ranges. The constant value of gauge factor in the whole strain range means good linearity of the strain sensor. The good linearity of the stain sensor is one of the important properties to measure the external stimuli. In general, the linearity of the strain sensor to the tensile strain could be explained by the value of adjust R−square used in the statistics. [29],[41],[55],[57] Except some strain sensors showing good linearity, many stain sensors reported for thin film type underwent low linearity of response on external stimuli. Although some reports did not include the value of adjust R−square, the resistance variation during stretching test had non−linear behavior. [19],[24],[30] This means that additional program or revision is required to confirm the applied strain exactly. The value of adjust R−square of our strain sensor were 0.99452~0.99763; this means the strain sensor showed good response on the external stress. Although little relaxations were observed at releasing state, the increasing−decreasing curve during stretching cycle was symmetric to the tensile strain.

The cycling number of tensile strain test was up to 1,000 times to confirm the durability of the strain sensor, the maximum value of normalized resistance for strain up to 50% of the strain sensor rarely changed as shown in figure 4.7. When we saw the resistance variation during one cycle exhibited in this figure, it was symmetric to the tensile strain. The excellent durability of the strain sensor resulted from crack bridging is a merit of the nanotube−based thin film as introduced in previous chapter. Moreover, the durability was well−maintained if a maximum tensile strain is constant. A low dependency about stretching speed is also critical factor for high feasible strain sensor to various applications such as data glove, shoes and cloth that required dynamic motion. But, only a few paper studied the effect of stretching speed that should be considered to detect the dynamic motion. [19] We also measured the resistance variation of the strain sensor during stretching cycle with various stretching speeds from 1 mm/min to 500 mm/min. The normalized resistances during stretching cycle were well matched except stretching speed of 500 mm/min that has only few measured results. Although an little inconsistency is observed during releasing the strain sensor, it showed stretching speed-independent response; this means the strain sensor is effective device to measure dynamic action.



	10%-stretched	30%-stretched	50%-stretched
Adj. R-square	0.99452	0.99763	0.99749
Gauge factor	10.92	12.94	12.33

Fig. 4.6 (a) Normalized resistance variations of 5-layer printed

SWCNT thin film having pre-pattern (w: 0.1 mm, n: 80) (open triangle) on PDMS substrate for strain up to (a) 10, (b) 30, and (c) 50% respectively and comparison results of 5-layer printed SWCNT thin film having no pattern (w: 0 mm, n: 0, rinsed sample-opened square, nitric acid treated sample-closed square)

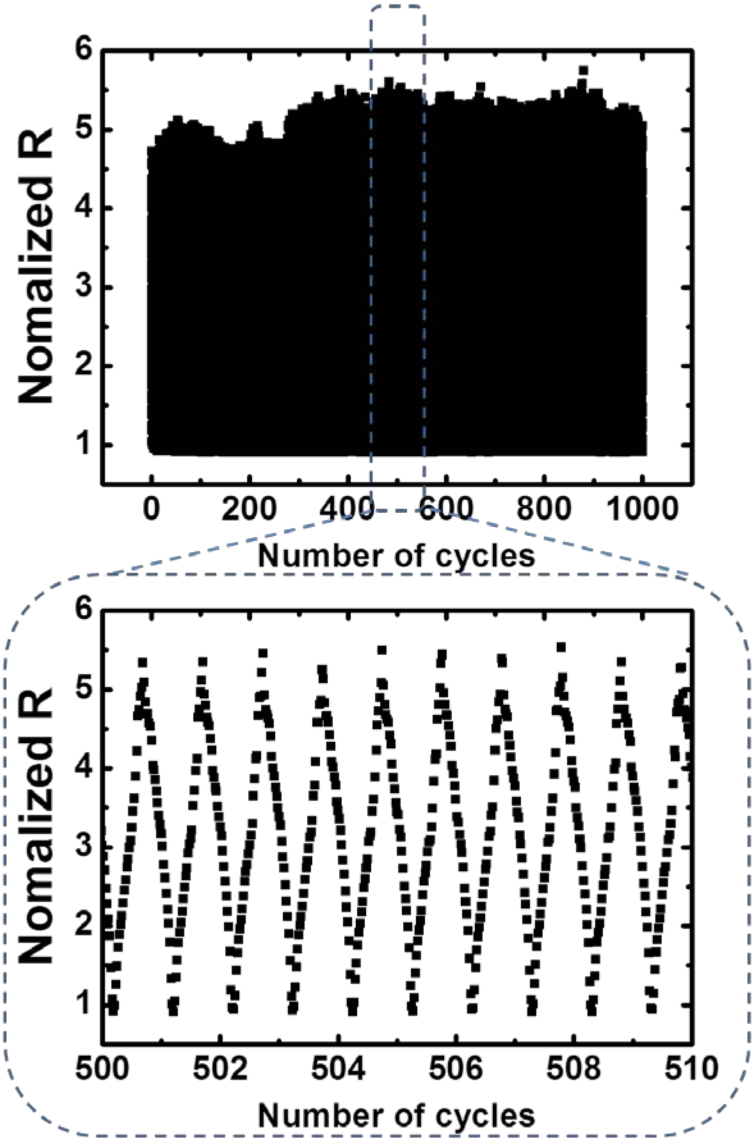


Fig. 4.7 Normalized resistance variation of 5-layer printed SWCNT thin film having pre-pattern (w: 0.1 mm, n: 80) measured during cyclic test for strains up to 50% with stretching speed of 100 mm/min.

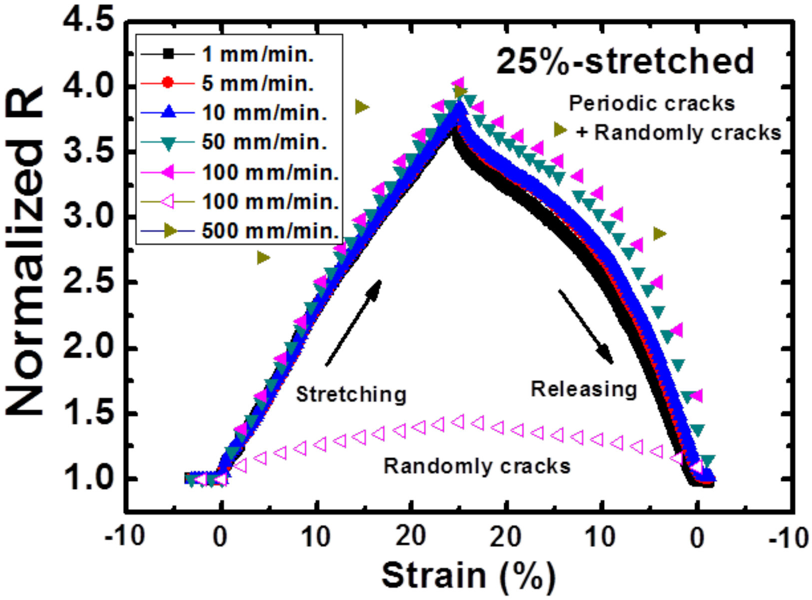


Fig. 4.8 Normalized resistance variation of 5−layer printed SWCNT thin film having pre−pattern (w: 0.1 mm, n: 80) for strains up to 25% with different stretching speed from 1 to 500 mm/min. (closed symbol) and comparison results of 5−layer printed SWCNT thin film have no pattern (w: 0 mm, n: 0) with stretching speed of 100 mm/min. (opened symbol)

4.4 Application of the inkjet-printed strain sensor

To confirm the feasibility of the strain sensor in various conditions such as wide strain range, a strain sensor fixed on substrate by adhesive glue was tested for specific motions. The 5-layer printed strain sensor optimized by pre-printed pattern was used for the test and the strain sensor was pre-stretched for strain up to 50% before fixed. To reduce sample variations, we used the printed strain sensor with gauge factor of 13.98. Figure 4.9 shows various motions and the response of the strain sensor on the motions. In the figure, the range of the motion varied from a tiny strain, even un-attempted, on the back of hand during mouse click to a strain on the finger during grabbing. Since the strain sensors have been studied for motion detector, many applications such as finger, wrist, and balloon test were reported to measure the induced tensile strain. [34],[43],[64] But there were only a few papers that classified the different motions using a strain sensor. [50] We can classify the different motions due to the high sensitivity of the strain sensor from small strain to large strain. It was observed that human motions such as surface tension on the back of hand, wrist flexion and finger bending are lower than 25% because calculated strain from the gauge factor and normalize resistance in the figure did not exceed 50%. Our strain sensor, highly sensitive strain sensor in the strain up to 50% with good linearity to the tensile strain and low dependency on the stretching speed, is much effective for the strain range of human motions. In addition, the response to the tensile strain was not affected by deformation speed that means a certain deformation with different deformation speed could be measured as equally subjected strain as shown in figure 5.8 (a). Although little variation was shown in the results, the resistance variations during finger bending with different speeds showed similar results. The inkjet-printed strain sensor is highly suitable for measuring various human motions based on different ranges and speeds.

A strain sensor system could be fabricated by the strain sensor and the stretchable electrode that has low sensitivity to the tensile strain. Some efforts for the strain sensor system have been tried to measure a spatial distribution of tensile strain under deformation conditions. [54] To obtain exact strain, resistance variation of the stretchable electrode should be lower under tensile strain unlike that of the strain sensor. It was reported that different materials and additional processes were required to meet the low resistance variation. But, an inkjet−printed strain sensor system reduces the laborious works resulted from materials and processes due to scalability of the inkjet printing system and selective enhancement in the strain−response. Figure 4.10 (a) illustrate strain sensor array on a glove; a strain sensor line with stretchable electrode was tested for detecting motion in the index finger. Periodically ordered patterns were also printed on the desirable region, which was a ligament placed between middle phalanx and proximal phalanx, in stretchable substrate, and then the sample was UV ozone treated. A long SWCNT line was printed on the sample and the sample was water−rinsed and nitric acid−treated. When the finger was bended, the resistance in the strain sensor line showed a drastic increase by finger motion on the region with periodically ordered patterns. The resistance in the strain sensor line showed a little increase by finger motion on the regions without the ordered patterns. The combination of stretchable electrode having low response on the tensile strain and strain sensor lines that have periodic patterns on different regions can measure spatial distribution of tensile strain during a certain motion.

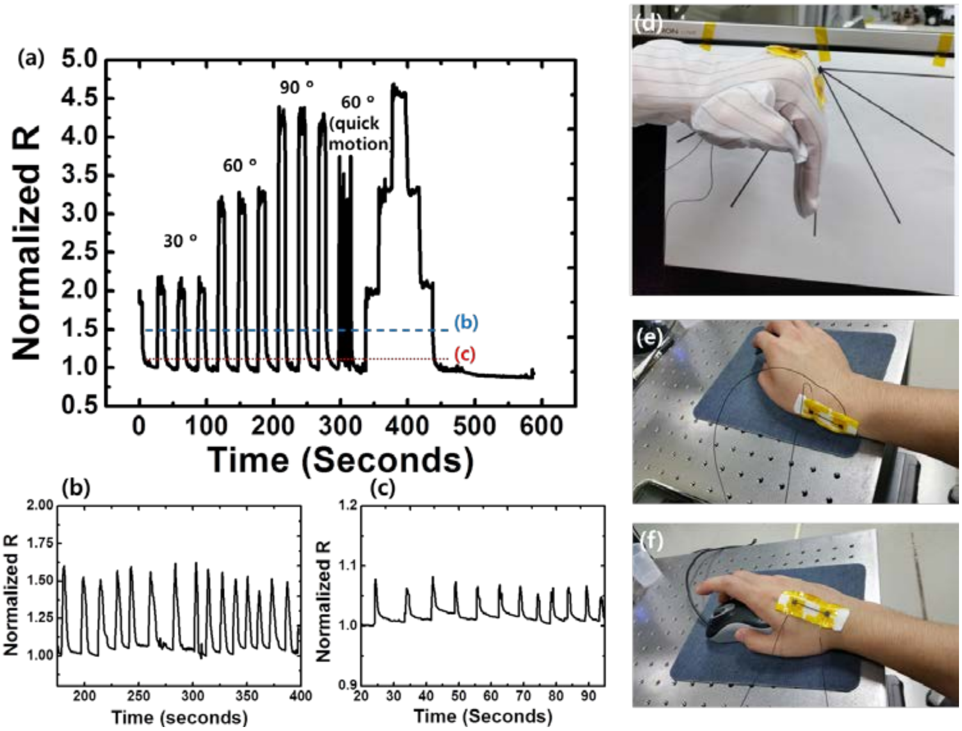


Fig. 4.9 Optical images and normalized resistance variation of 5-layer printed SWCNT thin film having pre-pattern (w: 0.1 mm, n: 80) measured in various actions at (a), (d) finger, (b), (e) wrist, and (c), (f) back of the hand, respectively.

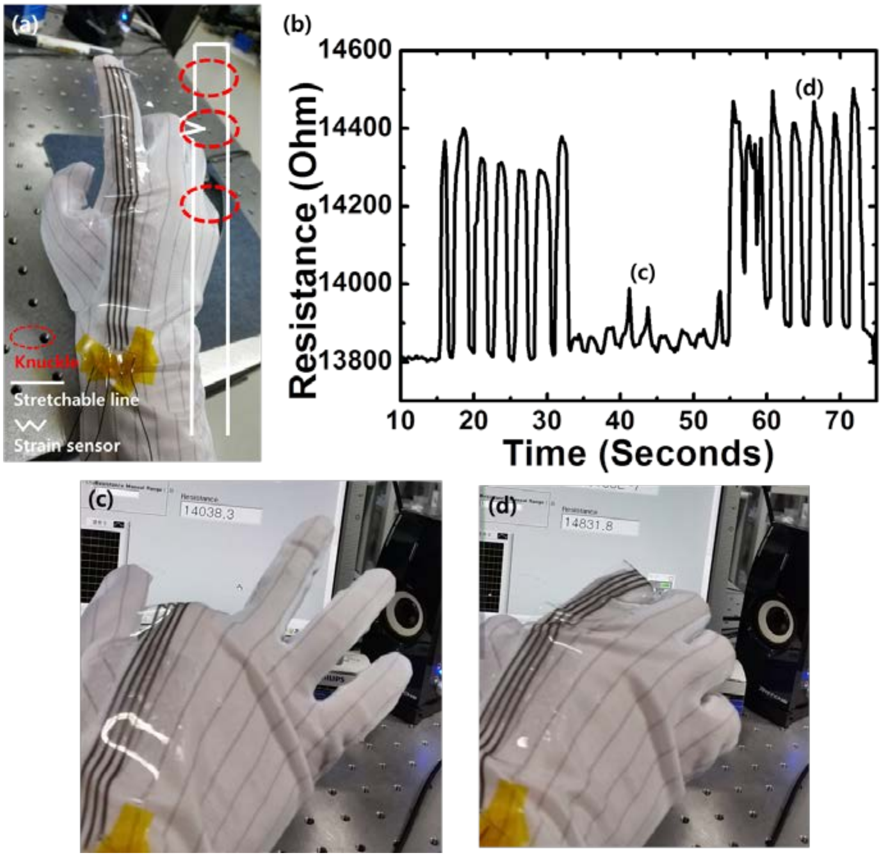


Fig. 4.10 (a) Optical image of combination of stretchable electrode and strain sensor (b) Resistance variation during the motion such as (c) bending fingertip and (d) grip

4.5 Conclusion

In summary, we fabricated inkjet-printed single-walled carbon nanotube thin films on stretchable substrate for the use of strain sensor having high response on the external strain. The strain sensor was fabricated using inkjet printer and the synthesized ink. Pre-pattern fabricated by inkjet printer caused large size crack; this is effective obstacle for the current flow under deformation. We confirmed that high response of strain sensor compared with reference sample not having pattern. The high response of strain sensor was optimized by the size and the number of the pre-pattern. The optimized strain sensor exhibited high strain range, high gauge factor, linear response on the tensile strain, high durability in cyclic test, and low variation resulted from different stretching speed. The properties of the inkjet-printed strain sensor were suitable to measure human motion having dynamic action. We successfully demonstrated the strains sensor to measure various human motions from small vibration caused in back of the hand to large change such as finger bending. We combined the stretchable electrode and the strain sensor to minimize the measuring system, and it was also demonstrated.

Reference

[1] J. A. Rogers, T. Someya, and Y. Huang, “Materials and Mechanics for Stretchable Electronics” Science, vol. 327, pp. 1603−1607, 2010

[2] C. Yu, C. Masarapu, J. Rong, B. Wei, and H. Jiang, “Stretchable Supercapacitor Based on Buckled Single−Walled Carbon−Nanotube Macrofilms” Adv. Mater., vol. 21, pp. 4793−4797, 2009

[3] T. Sekitani and T. Someya, “Stretchable, Large−area Organic Electronics” Adv. Mater., vol. 22, pp. 2228−2246, 2010

[4] D. −H. Kim, J. −H. Ahn, W. M. Choi, H. −S. Kim, T. −H. Kim, J. Song, Y. Y. Huang, Z. Liu, C. Lu, and J. A. Rogers, “Stretchable and Foldable Silicon Integrated Circuits” Science, vol. 320, pp. 507−511, 2008

[5] T. Sekitani, H. Nakajima, H. Maeda, T. Fukushima, T. Aida, K. Hata, and T. Someya, “Stretchable active−matrix organic light−emitting diode display using printable elastic conductors” Nat. Mater., vol. 8, pp. 494−499, 2009

[6] K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J. −H. Ahn, P. Kim, J. −Y. Choi, and B. H. Hong, “Large−scale pattern

growth of graphene films for stretchable transparent electrodes” Nature, vol. 457, pp. 706–710, 2009

[7] K. –Y. Chun, Y. Oh, J. Rho, J. –H. Ahn, Y. –J. Kim, H. R. Choi, and S. Baik, “Highly conductive, printable and stretchable composite films of carbon nanotube and silver”, Nat. Nanotechnol., vol. 5, pp. 853–857, 2010

[8] T. Sekitani, Y. Noguchi, K. Hata, T. Fukushima, T. Aida, and T. Someya, “A Rubberlike Stretchable Active Matrix Using Elastic Conductors” Science, vol. 321, pp. 1468–1472, 2008

[9] I. M. Graz, D. P. J. Cotton, A. Robinson, and S. P. Lacour, “Silicone substrate with in situ strain relief for stretchable thin–film transistors”, Appl. Phys. Lett., vol. 98, 124101 (3pp) 2011

[10] A. Romeo, Q. Liu, Z. Suo, and S. P. Lacour “Elastomeric substrates with embedded stiff platforms for stretchable electronics” Appl. Phys. Lett., vol. 102, 131904 (5pp), 2013

[11] H. Huang and F. Spaepen, “Tensile testing of free–standing Cu, Ag and Al thin films and Ag/Cu multilayers” Acta mater., vol. 48, pp. 3261–3269, 2000

[12] S. P. Lacour, S. Wagner, Z. Huang, and Z. Suo, “Stretchable gold conductors on elastomeric substrate” Appl. Phys. Lett.. vol.

82, 2404 (3pp), 2003

[13] S. Chung, J. Lee, H. Song, S. Kim, J. Jeong, and Y. Hong, “Inkjet-printed stretchable silver electrode on wave structured elastomeric substrate” Appl. Phys. Lett., vol. 98, pp. 153110 (3 pp), 2011

[14] Y. Sun, S. E. Thompson, and T. Nishida, “Strain Effect in Semiconductors: Theory and Device Applications”, Springer, New York, 2010

[15] M. Liu, D. M. Frangopol, and S. Kim, “Bridge Safety Evaluation Based on Monitored Live Load Effects”, J. Bridge Eng., vol. 14, pp. 257-269, 2009

[16] S. Tadakaluru, W. Thongsuwan, and P. Singjai, “Stretchable and Flexible High-Strain Sensors Made Using Carbon Nanotubes and Graphite Films on Natural Rubber” Sensors, vol. 14, pp. 868-876, 2014

[17] http://www.vtsz.cz/en/strain-gauges.php

[18] A. L. Window, “Strain gauge technology” Elsevier Applied Science, London, 1992

[19] C. Mattmann, F. Clemens, and G. Troster, “Sensor for Measuring Strain in Textile” Sensors, vol. 8, pp. 3719-3732,

2008

[20] P. Slobodian, P. Riha, R. Benlikaya. P. Svoboda, and D. Petras, “A Flexible Multifunctional Sensor Based on Carbon Nanotube/Polyurethane Composite” IEEE Sensors Jounal, vol. 13, pp. 4045−4048, 2013

[21] V. Arumugam, M. D. Naresh, and R. Sanjeevi, “Effect of strain rate on the fracture behavior of skin” , J. Biosci., vol. 19, pp. 307−313, 1994

[22] C. H. Daly, and G. F. Odland, “Age−related Changes in the Mechanical Properties of Human Skin” J. Invest. Dermatol., vol. 73, pp. 84−87, 1979

[23] B. B. Edin, “Quantitative Analyses of Dynamic Strain Sensitivity in Human Skin Mechanoreceptors” J. Neurophysiol, vol. 92, pp. 3233−3243, 2004

[24] T. Yamada, Y. Hayamizu, Y. Yamamoto, Y. Yomogida, A. Izadi−Najfabadi, D. N. Futaba, and K. Hata, “A stretchable carbon nanotube strain sensor for human−motion detection” Nat. Nanotechnol., vol. 6, pp. 296−301, 2011

[25] D. Lee, H.P. Hong, C. J. Lee, C. W. Park, and N. K. Min, “Microfabrication and characterization of spray−coated single−

wall carbon nanotube film strain gauges” Nanotechnolohy, vol. 22, 455301 (6pp), 2011

[26] M. Hempel, D. Nezichm, J. Kong, and M. Hofmann, “A Novel Class of Strain Gauges Based on Layered Percolative Films of 2D Materials”, Nano Lett., vol. 12, pp. 5714-5718, 2012

[27] H. Zhao, Y. Zhang. P. D. Bradford, Q. Zhou, Q. Jia, F. -G. Yuan, and Y. Zhu, “Carbon nanotube yarn strain sensors”, Nanotechnology, vol. 21, 305502 (5pp), 2010

[28] D. J. Cohen, D. Mitra, K. Peterson, and M. M. Maharbiz, “A Highly Elastic, Capacitive Strain Gauge Based on Percolating Nanotube Networks” Nano Lett., vol. 12, pp. 1821-1825, 2012

[29] M. K. Njuguna, C. Yan, N. Hu, J. M. Bell, and P. K. D. V. Yarlagadda, “Sandwiched carbon nanotube film as strain sensor” Composites: Part B, vol. 43, pp. 2711-2717, 2012

[30] C. Yan, J. Wang, W. Kang, M. Cui, X. Wang, C. Y. Foo, K. J. Chee, and P. S. Lee, “Highly Stretchable Piezoresistive Graphene-Nanocelluose Nanopaper for Strain Sensors” Adv. Mater., vol. 26, pp. 2022-2027, 2014

[31] W. Yang, C. He, L. Zhang, Y. Wang, Z. Shi, M. Cheng, G. Xie, D. Wang, R. Yang, D. Shi, and G. Zhang, “Growth, Characterization,

and Properties of Nanographene" Small, vol. 8, pp. 1429−1435, 2012

[32] T. Q. Trung, N. T. Tien, D. Kim, M. Jang, O. J. Yoon, and N. −E. Lee, "A Flexible Reduced Graphene Oxide Field−Effect Transistor for Ultrasensitive Strain Sensing" Adv. Funct. Mater., vol. 24, pp. 117−124, 2014

[33] S. −H. Bae, Y. Lee, B. K. Sharma, H. −J. Lee, J. −H. Kim, and J. −H. Ahn, "Graphene−based transparent strain sensor" Carbon, vol. 51, pp. 236−242, 2013

[34] L. Cai, L. Song, P. Luan, Q. Zhang, N. Zhang, Q. Gao, D. Zhao, Z. Zhang, M. Tu, F. Yang, W. Zhou, Q. Fan, J. Luo, W. Zhou, P. M. Ajayan, and S. Xie "Super−stretchable, Transparent Carbon Nanotube−Based Capacitive Strain Sensors for Human Motion Detection, Scientific Reports, vol. 3, 3048 (8pp), 2013

[35] X. Li, R. Zhang, W. Yu, K. Wang, J. Wei, D. Wu. A. Cao, Z. Li, Y. Cheng, Q. Zheng, R. S. Ruoff, and H. Zhu, " Stretchable and highly sensitive graphene−on−polymer strain sensors" Scientific Reports, vol. 2, 870 (6pp), 2012

[36] X. Chen, X. Zheng, J. −K. Kim, X. Li, and D. −W. Lee, "Investigation of graphene piezoresistors for use ad strain gauge

sensors., J. Vac. Sci. Technol. B, vol. 29, 06FE01 (5pp), 2011

[37] N. –K. Chang, C. –C. Su, and S. –H. Chang, “Fabrication of single–walled carbon nanotube flexible strain sensors with high sensitivity” Appl. Phys. Lett., vol. 92, 063501 (3pp), 2008

[38] X. Wang, T. Li, J. Adams, and J. Yang, “Transparent, stretchable, carbon–nanotube–inlaid conductors enabled by standard replication technology for capacitive pressure, strain and touch sensors” J. Mater. Chem. A, vol.1, pp.3580–3586, 2013

[39] Z. Zhao, C. He, R. Yang, Z. Shi, M. Cheng, W. Yang, G. Xie, D. Wang, D. Shi, and G. Zhang, “ Ultra–sensitive strain sensors based on piezoresistive nanographene films” Appl. Phys. Lett., vol. 101, 063112 (5pp), 2012

[40] D. J. Lipomi, M. Vosgueritchian, B. C–K. Tee, S. L. Hellstrom, J. A. Lee, C. H. Fox, and Z. Bao, “Skin–like pressure and strain sensors based on transparent elastic films of carbon nantobues” Nat. Nanotechnol., vol. 6, pp. 788–792, 2011

[41] C. Lee, L. Jug, and E. Meng, “High strain biocompatible polydimethlysiloxane–based conductibe graphene and multiwalled carbon nanotube nanocomposite strain sensors” Appl. Phys. Lett., vol. 102, 183511 (5pp), 2013

[42] Y. Lee, S. Bae, H. Jang, S. Jang, S. –E. Zhu, S. H. Sim, Y. I. Song, B. H. Hong, and J. –H. Ahn, “Wafer−Scale Synthesis and Transfer of Graphene Films” Nano Lett., vol. 10, pp. 490−493, 2010

[43] S. Luo and T. Liu, “SWCNT/Graphene Nanoplatelet Hybrid Thin Films for Self−Temperature−Compensated, Highly Sensitive, and Extensible Piezoresistive Sensors, Adv. Mater., vol. 25, pp. 5650− 5637, 2013

[44] D. Lee, H. P. Hong, M. J. Lee, C. W. Park, and N. K. Min, “A prototype high sensitivity load cell using single walled carbon nanotube strain gauges” Sensors and Actuators A, vol. 180, pp. 120−126, 2012

[45] A. Bessonov,, M. Kirikova, S. Haque, I. Gartseev, and M. J. A. Bailey, “Highly reproducible printable graphite strain gauges for flexible devices” Sensors and Actuators A: Physical, vol. 206, pp. 75−80, 2014

[46] M. Li, H. Li, W. Zhong, Q. Zhao, and D. Wang, “Stretchable Conductive Polypyrrole/Polyurethane (PPy/PU) Strain Sensor with Netlike Microcracks for Human Breath Detection, ACS Appl. Mater. Interfaces, vol. 6, pp. 1313−1319, 2014

[47] G. Latessa, F. Brunetti, A. Reale, G. Saggio, and A. D. Carlo, “Pieoresistive behavior of flexible PEDOT:PSS based sensors” Sensors and Actuators B: Chemical, vol. 139, pp. 304−309, 2009

[48] C. Farcau, N. M. Sangeetha, H. Moreira, B. Viallet, J. Grisolia, D. C. –Pradines, and L. Ressier, “High−Sensitivity Strain Gauge based on a Single Wire of Gold Nanoparticles Fabricated by Stop−and−Go Convective Self−Assembly”, ACS NANO, vol. 5, pp. 7137−7143, 2011

[49] B. Ando and S. Baglio, “All−Inkjet Printed Strain Sensors” IEEE Sensors Journal, vol. 13, pp. 4874−4879, 2013

[50] X. Xiao, L. Yuan, J. Zhong, T. Ding, Y. Liu, Z. Cai, Y. Rong, H. Han, J. Zhou, and Z. L. Wang, “High−Strain Sensors Based on ZnO Nanowire/Polystyrene Hybridized Flexible Films” Adv. Mater. Vol. 23, pp. 5440−5444, 2011

[51] Y. Yang, W. Guo, J. Qi, and Y. Zhang, “Flexible piezoresitive strain sensor based on single Sb−doped ZnO nanobelts” Appl. Phys. Lett., vol. 97, 223107 (3pp), 2010

[52] V. Eswaraiah, K. Balasubramaniam, and S. Ramaprabhu, “One−pot synthesis of conducting graphene−polymer composites and their strain sensing application” Nanoscale, vol. 4, pp. 1258−

1262, 2012

[53] Y. Wang, R. Yang, Z. Shi, L. Zhang, D. Shi, E. Wang, and G. Zhang, "Super-Elastic Graphene Ripples for Flexible Strain Sensors" ACS NANO, vol. 5, pp. 3645-3650, 2011

[54] N. Lu, C. Lu, S. Yang, and J. A. Rogers, " Highly Sensitive Skin-Mountable Strain Gauges Based Entirely on Elastomers" Adv. Funct. Mater., vol. 22, pp. 4044-4050, 2012

[55] A. Ferrreira, J. G. Rocha, A. A.-Casaos, M. T. Martinez, F. Vaz, S. L. -Mendez, "Electromechanical performance of poly(vinylidene fluoride)/carbon nanotube composites for strain sensor applications" Sensor and Actuators A, vol. 178, pp. 10-16, 2012

[56] H. Gullapalli, V. S. M. Vemuru, A. Kumar, A. B. -Mendez, R. Vajtai, M. Terrones, S. Nagarajaiaj, and P. M. Ajayan, "Flexible Piezoeletric ZnO-Paper Nanocomposite Strain Sensor" Small, vol. 6, pp. 1641-1646, 2010

[57] S. -H. Hwang, H. W. Park, Y. -B. Park, M. -K. Um, J. -H. Byun, and S. Kwon, "Electromechanical strain sensing using polycarbonate-impregnated carbon nanotube-graphene nanoplatelet hybrid composite sheets" , Composites Science and

Technology, vol. 89, pp. 1−9, 2013

[58] L. Hu, J. W. Choi, Y. Yang, S. Jeong, F. L. Mantia, L. -F. Cui, and Y. Cui, “Highly conductive paper for energy−storage devices” Proc. Natl. Acad. Sci. USA, vol. 106, pp. 21490−21494, 2009

[59] M. F. Islam, E. Rojas, D. M. Bergey, A. T. Johnson, and A. G. Yodh, “High Weight Fraction Surfactant Solubilization of Single−Wall Carbon Nanotubes in Water” Nano Lett, vol. 3, pp. 269−273, 2003

[60] T. Takenobu, N. Miura, S. -Y. Lu, H. Okimoto, T. Asano, M. Shiraishi, and Y. Iwasa, “Ink−Jet Printing of Carbon Nanotube Thin−Film Transistors on Flexible Plastic Substrate” Appl. Phys. Express, vol. 2, 025005 (3pp), 2009

[61] M. E. Launey and R. O. Ritchie, “on their Fracature Toughness of Advanced Materials” Adv. Mater., vol. 21, pp. 2103−2110, 2009

[62] S. Zhang, D. Sun, Y. Fu, and H. Du, “Toughening of hard nanostructural thin films: a critical review” Surf. Coat. Technol., vol. 198, pp. 2−8, 2005

[63] W. Zhang, R. C. Picu, and N. Koratkar, “Suppression of

fatigue crack growth in carbon nanotube composites” Appl. Phys. Lett., vol. 91, 193109 (3pp), 2007

[64] S. H. Nam, P. J. Jeon, S. W. Min, Y. T. Lee, E. Y. Park, and S. Im, “Highly sensitive Non−Classical Strain Gauge Using Organic Heptazole Thin−Film Transistor Circuit on a Flexible Substrate, Adv. Funct. Mater., Online Published, 2014

[65] N. Hu, Y. Karube, C. Yan, Z. Masuda, and H. Fukunaga, “Tunneling effect in a polymer/carbon nanotube nanocomposite strain sensor” Acta Materialia, vol. 56, pp. 2929−2936, 2008

Chapter 5

Conclusion

In this thesis, we report the inkjet-printed single-walled carbon nanotube thin films on stretchable substrate for stretchable electrode and strain sensor. The carbon nanotube is well known materials as excellent properties in term of electrical and mechanical properties resulting in various applications exhibiting high performance. Nevertheless the high performance in the various applications, some technical issues of the carbon nanotube such as scalability and low dispersion stability in aqueous solution having high safety solvent than organic solvent disturb the use of carbon nanotube. Especially, it has many problems for the use in stretchable electronic, known as next generation electronics, requiring large area device, compatibility with polymer material. We tried to solve the technical issues of the carbon nanotube using the inkjet printer and synthesized single−walled carbon nanotube ink. To use the synthesized ink for inkjet printing, some conditions were optimized. In the optimized condition, inkjet−printed single−walled carbon nanotube showed well−shaped films and the printed films were developed for stretchable electrode and strain sensor using specific phenomenon of the carbon nanotube.

The carbon nanotube has advantage in term of the properties of the carbon nanotube, but it has also disadvantage of low dispersion properties in aqueous solution compatible with stretchable substrate. To use the aqueous solution, we fabricated single−walled carbon nanotube ink using surfactant, water, and nanotube powder. In fabrication process, we used tip sonication, ultracentrifugation, and filtration. The tip sonication improved the effect of the surfactant in the solution by untangling nanotube, and the ultracentrifugation and filtration prevent a large bundle of carbon nanotube clogging a nozzle on cartridge of the inkjet printer. Since the printed ink has hydrophilic properties that are not matched with the PDMS substrate having hydrophobic properties, we used the UV ozone treatment and controlled the substrate temperature of the inkjet printer. The treatment and the effect of surfactant used for dispersion stability showed a significant improvement of film properties. Two post treatments were performed to the printed film having a lot of surfactant that reduce the electrical properties of the thin film. Water rinsing reported by an effective method to reduce the surfactant in the thin film and nitric acid treatment improving the electrical properties of carbon nanotube exhibited a drastic change in electrical and structural properties of the thin film.

The printed single-walled carbon nanotube thin film showed excellent mechanical properties. After the post treatments that were performed for reducing the surfactant in the thin film, the thin film had improved electrical and mechanical properties. Unlike a untreated sample having a high resistance and a large variation in resistance during stretching test, the sample performed by two post treatment had good electrical properties and excellent mechanical properties. Except initial increase in resistance, the resistance variation of the treated sample had low value under tensile strain. The specific phenomenon was maintained although strain range, stretching speed, and the number in cyclic test changed. It was originated from the structure of the single-walled carbon nanotube thin film. The printed thin film had tangled structure of the single−carbon nanotube, which disturb crack propagation. When a crack occurred in the thin film, it was propagated to the whole thin film by external stress. But the tangled carbon nanotubes prevent the crack propagating, which related the excellent mechanical properties of single−walled carbon nanotube. The high strechability of the printed thin film demonstrated via integration with light−emitting diode.

The resistance response on the tensile strain changed the status of the thin film. The nitric acid treated thin film had low response on the tensile strain; this is suitable for the stretchable electrode. In contrast with the nitric acid treatment, pre−pattern perform by inkjet printer caused large scale crack under deformation; this large crack narrow the current path in the thin film. The intended crack improved the resistance response on the tensile strain significantly. The number of crack and size were optimized using the pre−pattern, the optimized thin film had high response on the tensile strain, and the response was maintained during stretching tests. The excellent strain response was also obtained with different stretching speed and high cycling number in stretching test. It was successfully demonstrated via various motion tests such as finger and wrist bending, and mouse clicking. In addition, the strain sensor having high response on the tensile strain and the stretchable electrode having low response on the tensile stain were combined. The combination of strain sensor and stretchable electrode was also demonstrated.

Publication and Conference Presentation

International Journal

3. T. Kim, H. Song, J. Ha, S. Kim, D. Kim, S. Chung, Y. Hong*, "Inkjet-Printed Stretchable Single-Walled Carbon Nanotube Electrodes with Excellent Mechanical Properties" Appl. Phys. Lett., vol. 104, 113103 (4pp), 2014 **(highlighted in Nature, vol. 508, p. 291, 2014)**

2. S. Kim, J. Byun, S. Choi, D. Kim, **T. Kim**, S. Chung, Y. Hong*, "Negatively Strain-Dependent Electrical Resistance of Magnetically Arranged Nickel Composites: Application to Highly Stretchable Electrodes and Stretchable Lighting Devices", Adv. Mater., vol. 26, pp. 3094-3099, 2014 **(Cover image paper)**

1. J. Jeong, M. Kim, S. Lee, D. Kim, **T. Kim**, and Y. Hong*, "Self-Defined Short Channel Formation with Micromolded Separator and Inkjet-printed Source/Drain Electrodes in OTFTs", IEEE Electron Device Letters, vol, 32, 1758 (3pp), 2011

International Conference Presentation

5. T. Kim, Y. Joo, S. Kim, J. Byun and Y. Hong*, "A highly sensitive and repeatable strain sensor based on inkjet−printed single walled carbon nanotube", 2013 MRS Spring meeting, San Francisco, USA, April 1−5, 2013

4. T. Kim, J. Byun, H. Song and Y. Hong*, "Inkjet−printed SWCNT films for stretchable electrode and strain sensor applications", 70th Device Research Conference, Pennsylvania, USA, June 18−20, 2012

3. T. Kim, H. Song, J. Lee, and Y. Hong*, "Inkjet−printed Single Walled Carbon Nanotube Electrode for Stretchable Electronics" , Material Research Society, Boston, USA, Nov. 28−Dec. 2, 2011

2. K. I. Lee, S. U. Byun, J. H. Han, K. W. Shin, S. H. Kim, C. S. Lee, **T.−H. Kim**, and Y. Hong*, "Fine Patterning of Carbon Nanotube by Electrohydrodynamic Printing" , NT11 International Conference on the Science and Application of Nanotubes, Cambridge, UK, July 10−16, 2011

1. T.−H. Kim, H. D. Yoo, S. M. Oh, and Y. Hong*, "Inkjet−printed Single Walled Carbon Nanotube Electrode of Supercapacitors for Flexible Application" , NT11 International Conference on the Science and Application of Nanotubes, Cambridge, UK, July 10−16, 2011

국문 초록

최근 센서, 박막 트랜지스터, 유기 발광 소자 등 다양한 분야에서 신축성 전자소자들이 소개되고 있다. 이러한 신축성 전자소자의 급격한 성장은 재료, 소자 물리, 화학, 기계공학 등 다양한 분야의 협업을 통해 이루어지고 있다. 지속적으로 기존의 신축성 전자소자가 지닌 문제점을 해결하고, 우수한 특성을 지닌 신축성 전자소자를 개발하기 위해서는 다방면으로 접근하여 넓은 시각에서 바라볼 필요가 있다. 현재 신축성 전자소자를 제작하기 위해서는 높은 기계적 변형을 견딜 수 있는 재료, 구조, 시스템이 필요하며, 그 중에서도 가장 기본이 되는 우수한 기계적 특성의 가진 재료의 선정은 필수적이다.

탄소나노튜브는 신축성 전자소자에서 가장 각광받는 재료 중 하나이다. 독특한 튜브구조와 그로부터 기인한 높은 기계적, 전기적 특성은 신축성 전자소자를 제작하기 위한 최적의 특성을 보여주고 있다. 또한, 관능기를 이용한 기계적, 전기적 특성 조절이 용이하고, 외부 자극에 대한 반응이 변화하는 점은 탄소나노튜브의 가장 큰 장점이며, 다양한 전자소자 제작을 가능하게 한다. 하지만, 개별 탄소나노튜브 대비 낮은 박막 특성을 가지며 탄소나노튜브의 높은 합성비용으로 인해 스크린 프린팅과 같이 재료의 소모가 큰 대면적 제작공정에 적합하지 않고, 물

기반의 잉크에 낮은 분산 안정성을 보여 신축성 전자소자 대면적 제작에 많은 문제점을 나타내고 있다.

이를 해결하기 위해 재료의 소모가 적은 잉크젯 프린팅 공정을 이용하여 탄소나노튜브 기반 신축성 전자소자 제작을 진행하였다. 잉크젯 프린팅 공정은 공정비용이 저렴하며, 대면적 전자소자 제작이 용이하며, 재료의 소모가 적은 장점을 가지고 있지만, 사용되는 잉크의 점도에 영향을 많이 받아 재료 사용의 제약이 있다는 단점을 지니고 있다. 유해성이 높은 유기용매가 아닌 물을 이용하여 직접 잉크를 제조하여 앞서 언급된 단점을 해결하고, 계면활성제를 이용하여 낮은 분산성을 해결하였다. 기판온도 최적화와 UV(ultraviolet) 오존을 이용한 표면처리를 이용하여 잉크젯 프린팅 기반 탄소나노튜브 박막을 제작하였다. 분산성을 향상시키기 위해 이용된 계면활성제는 탄소나노튜브 박막의 전기적 특성을 저해시키기 때문에, 인쇄된 박막 내부의 계면활성제를 줄이는 과정이 필요하다. 본 연구에서는 물을 이용한 계면활성제를 씻어내고 묽은 질산을 이용하여 추가적인 전기적 특성 향상을 유도하였다. AFM (Atomic Force Microscope)를 이용하여 두 가지의 후처리 공정 동안 발생하는 구조적 변화를 확인하였으며, 5 번 인쇄된 박막의 면저항이 313.55 Ω/□에서 19.08 Ω/□으로 급감하는 것을 확인하였다.

앞서 제작된 잉크젯 프린팅 공정 기반 탄소나노튜브 박막은 높은 기계적 변형률 (100%)에서도 파괴되지 않는 것이 확인되었다. 높은 기계적

변형속도(100 mm/min.)의 반복 인장 실험에서도 박막이 파괴되지 않고, 전기적 특성이 일정하게 유지하는 것을 확인하였다. 비록 미세한 전기적 특성 변화가 발생하지만, 반복 인장 실험에서도 전기적 특성이 유지되는 현상은 다양한 실험조건에서 발생한다. 이는 SEM (Scanning Electron Microscope)와 현미경 관찰을 통해 균열 브릿징 현상에 의해 기인하는 것을 확인하였다. 잉크젯 프린팅 기반 탄소나노튜브 박막의 우수한 기계적 특성을 활용하기 위하여 LED (Light- Emitting Diode) 램프를 연결하여 기계적 변형 동안 램프의 밝기 변화를 측정하였으며, 램프의 밝기가 일부 변화하였지만 높은 기계적 변형에서도 유지되는 것을 확인하였다.

외부의 기계적 변형에 의한 잉크젯 프린팅 기반 탄소나노튜브 박막의 전기적 특성 변화는 박막의 구조적 변화를 이용하여 쉽게 조절할 수 있다. 선-인쇄된 탄소나노튜브 패턴을 이용하여 박막 내부의 균열을 인위적으로 유도하고, 균열의 크기나 방향을 조절하여 박막의 기계적 특성은 유지하되 전기적 특성 변화를 크게 증가시킬 수 있다. 선-인쇄된 탄소나노튜브 패턴의 크기나 모양을 최적하여 높은 민감도와 높은 신뢰성, 그리고 우수한 선형성을 가진 잉크젯 프린팅 공정 기반 변형률 감지 센서를 제작하였다. 제작된 센서를 이용하여 사람의 다양한 움직임을 측정 가능한 것이 확인되었다. 앞서 제작된 신축성 전극과 변형률 감지 센서는 간단한 처리공정으로 외부 변형에 의한 전기적 특성

변화율이 상반되게 변화하는 것을 이용하였으며, 신축성 전극과 변형률 감지 센서를 통합한 변형률 감지 시스템을 제작 가능성을 확인하였다.

주요어 : 잉크젯 프린팅, 단일벽 탄소나노튜브, 신축성, 변형률 감지센서
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