The invented ink-jet printing method for the construction of thin film transistors using all SWNTs on flexible plastic films is a new process. This method is more practical than all of existing printing methods in the construction TFT and RFID tags because SWNTs have superior properties of both electrical and mechanical over organic conducting oligomers and polymers which often used for TFT. Furthermore, this method can be applied on thin films such as paper and plastic films while silicon based techniques can not used on such flexible films. These are superior to the traditional conducting polymers used in printable devices since they need no dopant and they are more stable. They could be used in conjunction with conducting polymers, or as stand-alone inks.

19 Claims, 7 Drawing Sheets

The references cited as follows:

U.S. PATENT DOCUMENTS

FOREIGN PATENT DOCUMENTS
KR 1020060106023 4/2008
WO 04/001860 12/2003

OTHER PUBLICATIONS

The abstract reads:

The invented ink-jet printing method for the construction of thin film transistors using all SWNTs on flexible plastic films is a new process. This method is more practical than all of existing printing methods in the construction TFT and RFID tags because SWNTs have superior properties of both electrical and mechanical over organic conducting oligomers and polymers which often used for TFT. Furthermore, this method can be applied on thin films such as paper and plastic films while silicon based techniques can not used on such flexible films. These are superior to the traditional conducting polymers used in printable devices since they need no dopant and they are more stable. They could be used in conjunction with conducting polymers, or as stand-alone inks.

19 Claims, 7 Drawing Sheets
U.S. PATENT DOCUMENTS

OTHER PUBLICATIONS
* cited by examiner
Functionalized SWNT

3M Transparency film

Printing
HP Deskjet 3845

Gate: 4 K Ohm / sq
(SWNTs)

PMMA
Bar coating

Dielectric layer

Functionalyzed SWNT

Printing
HP Deskjet 3845

Drain and Source
(SWNT bundles)

FIGURE 1
RFID tag lay out

[Block diagram of the designed transponder IC (Tag)]

Ring oscillator

Fig. 4
5 stage ring oscillator
printing sequences

Fig. 5

Step (a)
Gate, wire: bundle SWNT

Step (b)
Insulator: PMMA

Step (c)
Drain and source, wire: bundle SWNT

Step (d)
Active layer: functionalized SWNT

5 stage ring oscillator
Construction of Memory is in processing using FET and Floating gate transistor

- 4-bit * 4-bit NOR based ROM array

Fig. 6
FIGURE 7
FIGURE 8
PREPARATION OF THIN FILM TRANSISTORS (TFTs) OR RADIO FREQUENCY IDENTIFICATION (RFID) TAGS OR OTHER PRINTABLE ELECTRONICS USING INK-JET PRINTER AND CARBON NANOTUBE INKS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority to and benefit of U.S. Provisional Application Ser. No. 60/739,666, filed on Nov. 23, 2005, entitled: PREPARATION OF THIN FILM TRANSISTORS (TFTs) OR RADIO FREQUENCY IDENTIFICATION (RFID) TAGS OR OTHER PRINTABLE ELECTRONICS USING INK-JET PRINTER AND CARBON NANOTUBE INKS, by inventor Gyou-Jin Cho, et al. The present application further claims priority to and benefit of U.S. Provisional Application Ser. No. 60/775,060, filed on Feb. 21, 2006, entitled: PREPARATION OF THIN FILM TRANSISTORS (TFTs) OR RADIO FREQUENCY IDENTIFICATION (RFID) TAGS OR OTHER PRINTABLE ELECTRONICS USING INK-JET PRINTER AND CARBON NANOTUBE INKS, by inventor Gyou-Jin Cho, et al. The aforementioned provisional applications are hereby incorporated herein by reference.

FEDERALLY-SPONSORED RESEARCH

This invention was made, in part, with support from the Office of Naval Research, Grant No. N00014-04-1-0765. The U.S. Government has certain rights in the invention.

FIELD OF THE INVENTION

The present invention relates generally to printable electronics, more particularly to printable electronics made using ink jet printers and carbon nanotube inks.

BACKGROUND OF THE INVENTION

As the demand for ubiquitous electronics is largely consumer driven, in some fields factors such as disposability, low cost and massive market applications are tending to become more important than ultrapowerful microelectronic devices. Therefore, macroelectronic devices that are light, inexpensive, flexible, disposable, and minimally sufficient to execute the simple task at hand are in high demand. Inexpensive radio frequency identification tags, flexible displays, disposable cell phones and e-papers are among the potential applications of such devices. To make practical use of these applications, it is desirable that their components are prepared using simple and inexpensive means that do not require using high vacuum deposition or photolithography facilities.

BRIEF DESCRIPTION OF THE INVENTION

The invented ink-jet printing method for the construction of thin film transistors using all SWNTs on flexible plastic films is a new process. This method is more practical than all of exiting printing methods in the construction TFT and RFID tags because SWNTs have superior properties of both electrical and mechanical over organic conducting oligomers and polymers which often used for TFT. Furthermore, this method can be applied on thin films such as paper and plastic films while silicon based techniques can not used on such flexible films. These are superior to the traditional conducting polymers used in printable devices since they need no dopant and they are more stable. They could be used in conjunction with conducting polymers, or as stand-alone inks.

According to some embodiments, a process for making thin film (TF) electronic devices comprising the steps of: using an ink jet printer mechanism to print electronic device patterns on a substrate as a composite ink mixture of metallic carbon nanotubes (m-NTs) and semiconductor carbon nanotubes (s-NTs), wherein the m-NTs are active and dominate the characteristics of the composite ink mixture in any of the electronic device patterns designated as a conductor patterns; de-activating a portion of the m-NTs in any of the electronic device patterns designated as resistive device patterns; and de-activating substantially all of the m-NTs in any of the electronic patterns designated as semiconducting device patterns.

According to some embodiments, a thin film electronic circuit, comprises a circuit formed on a substrate to have a pre-determined functionality requiring conductors interconnecting a plurality of resistive devices, capacitive devices, inductive devices, and active semiconductor devices, wherein the conductors, the resistive devices, the capacitive devices, the inductive devices, and the active semiconductor devices are formed at least in part by the process of: using an ink jet printer mechanism to print electronic device patterns on a substrate, as a composite ink mixture of metallic carbon nanotubes (m-NTs) and semiconductor carbon nanotubes (s-NTs), wherein the m-NTs are active and dominate the characteristics of the composite ink mixture in any of the electronic device patterns designated as the conductors; de-activating a portion of the m-NTs of the composite ink mixture in any of the electronic device patterns designated in the resistive devices; and de-activating substantially all of the m-NTs of the composite ink mixture in any of the electronic patterns designated as a semiconducting portion of the active semiconductor devices.

According to some embodiments, a thin film transistor (TFT) comprises: a channel fabricated as a first layer of a composite ink mixture of metallic carbon nanotubes (m-NTs) and semiconductor carbon nanotubes (s-NTs) applied to a substrate, wherein the m-NTs dominate the characteristics of the composite ink mixture and are de-activated in-situ to render the channel a semiconductor channel layer; a gate area fabricated by applying a dielectric layer over a portion of the semiconductor channel layer while exposing a source area and a drain area on the semiconductor channel layer; and a gate electrode, a source electrode and a drain electrode fabricated as electrode layers of the composite ink mixture applied to the gate area, the source area, and the drain area, wherein the m-NTs of the composite ink mixture of the electrode layers are not de-activated thus rendering the electrode layers of the composite ink mixture substantially conductive, wherein a conductivity of the channel is modulated in response to voltage applied to the gate electrode.

The foregoing has outlined rather broadly the features and technical advantages of a number of embodiments of the present invention in order that the detailed description of the present invention that follows may be better understood. Additional features and advantages of the invention will be described hereinafter.

BRIEF DESCRIPTION OF THE DRAWINGS

For a more complete understanding of the present invention, and the advantages thereof, reference is now made to the following descriptions taken in conjunction with the accompanying drawings, in which:
Applications to thin-film transistors that use single-walled carbon nanotube (SWNT) based films for use in TFTs or other electronic devices, such as paper and plastic films while silicon-based techniques cannot maintain consistent values for printed devices under ambient conditions.


With regard to the present invention, the unique aspect about the technique described herein is the deactivation (lowering of the conductivity) of the metallic SWNTs by functionalization of the mixed SWNT samples. By employing such deactivation, none of the functionalized SWNTs need to be removed from the sample. They can be left in the sample. The semiconductor tubes then dominate the properties of the active (semiconductive) layers. It may be that the functionalization of the metallics causes them to become poor conductors or themselves semiconductors; regardless of their properties, as long as the metallics lose their metallic character, the overall sample is useful as the active layer. None of the other above-cited published works covalently functionalize the SWNTs in order to modulate their conductive properties and thereby render them useful as active layers.

We detail herein new ways to address the obstacles involved in using a combination of SWNT inks and an ink-jet method. (Herein, the prefix “m” denotes metallic in conductive properties, and the prefix “s” denotes semiconducting in conductive properties, and that which is applied to TFTs could likewise be applied to RFID tags and other printable structures). In principle, if we could make pure m-SWNTs and pure s-SWNTs, we could use m-SWNT to fabricate the electrodes (i.e., source, drain and/or gate) of the TFTs and s-SWNTs to fabricate the active layer (semiconductive layer between the source-drain and above the dielectric layer) of the TFTs. Note that we have also made dielectric layers from heavily fluorine-functionalized SWNTs, but they were unstable, hence we use more conventional dielectrics, such as PMMA for that layer. Since SWNTs in general are known to have a strong affinity for plastic surfaces and for other SWNTs, printed coatings containing either m-SWNTs or s-SWNTs should adhere both to the substrate and to each other. However, methods for reliably producing or segregating pure m-SWNTs from s-SWNTs have yet to be developed. Hence, in this work we used the native mixture of SWNTs (mixture of the metallic and semiconductors wherein the metallic dominate the behavior) for the electrodes and a product enriched in s-SWNTs (ps-SWNTs), prepared by selective functionalization (see, e.g., Dyke, C. A.; Stewart, M. P.; Tour, J. M. “Separation of Single-Walled Carbon Nanotubes on Silica Gel. Materials Morphology and Raman Excitation Wavelength Affect Data Interpretation,” J. Am. Chem. Soc. 2005, 127, 4497-4509; Hudson, J. L.; Casavant, M. J.; Tour, J. M. “Water-Soluble, Exfoliated, Nonroping Single-Wall Carbon Nanotubes,” J. Am. Chem. Soc. 2004, 126, 11158-11159; Dyke, C. A.; Tour, J. M. “Feature Article: Covalent Functionalization of Single-Walled Carbon Nanotubes for Materials Applications,” J. Phys. Chem. A. 2004, 108, 11151-11159; Strano, M. S.; Dyke, C. A.; Usrey, M. L.; Barone, P. W.; Allen, M. J.; Shan, H.; Kittrell, C.; Hauge, R. H.; Tour, J. M.; Smalley, R. E. “Electronic Structure Control of Single Walled Carbon Nanotube Functionalization,” Science 2003, 301, 1519-1522) for the active layer. Finally, unlike typical conducting polymers, SWNTs are inherently conductive and require no dopants.

In an exemplary embodiment, for the fabrication of electrodes of a TFT, 0.37 g of crude SWNT bundles (HiPco) are dispersed in 1 L of water/SDS (10 g) using an ultrasonic homogenizer (Polyscience X-520, 750-Watt) for 1 h; then to 20 mL of the dispersion is added 2 mL decanol (water to decanol 10:1 ratio), and the decanol is mixed with the dispersed SWNT bundles under sonication for 30 min using an ultrasonic cleaner (Cole-Parmer: B3-R). The resulting mix-
sures are filtered (cotton-packed column) to remove aggregated SWNTs, and the filtrate is used as a conducting ink. The gate electrodes are printed on the transparent film by using the ink-jet printer with the cartridge refilled by the prepared SWNTs ink. To attain the lowest surface resistance for printed electrodes, the deposition cycle (printing, drying, and washing with ethanol to remove the surfactant and decanol) is repeated 10 times. The printed gate electrodes have a surface resistance of 4 KΩ/sq, which is the lowest surface resistance obtained with given SWNTs and our printing system. As shown in atomic force microscopy (AFM) images of the gate electrode, SWNT bundles are well-packed and well-adhered on the surface so that it is difficult to remove even by the Scotch™ tape test.

The gate dielectric layer is then coated on the gate using a solution containing 1 g of poly(methyl methacrylate) (M₉ 120,000) in 10 ml of 2-butanone and a bar coater. The PMMA-coated film is annealed for 2 h at 110-120°C under ambient conditions and then the drain and source electrodes are printed on the film using the same conducting SWNTs ink and same printing cycles (10 times). Since our printing system has a maximum resolution of 300 μm, the channel length of the all-SWNT-TFTs are printed at 800 μm to prevent a short between the drain and source electrodes. The surface resistance of the printed drain, source, and gate electrodes are approximately equivalent.

For the deposition of ps-SWNTs as the active layer, we first prepare ps-SWNTs by selectively reacting the m-SWNTs from an aqueous dispersion of individual SWNTs (crude HiPco, 0.07 g/L). Since the HiPco process affords samples containing ca. 50 different tube types with ca. one third of m-SWNT and two thirds of s-SWNT, we need to enrich s-SWNT from the solution through the selective deactivation of m-SWNT. Since we previously showed the p-nitrobenzenediazonium tetrafluoroborate can preferentially react with m-SWNTs, we can deactivate them to some degree via the surface functionalization reaction. When functionalized, the m-SWNTs are assumed to be poor conductors. The selective functionalization of m-SWNT is monitored by UV/vis/NIR to confirm the reduction of intensity for van Hove singularities.

The solution of ps-SWNT is formulated with water/decanol as before. The active layer, with a width of 2600 μm and channel length of 800 μm, is printed 5 times following the same printing cycles (printing, drying, and washing with ethanol to remove surfactant and decanol) as the electrodes except using the ps-SWNT ink.

All electrical measurements for printed SWNT-TFT are carried out under ambient conditions using a semiconductor parameter analyzer (Agilent 4155C).

The methods of the present invention can be directly used in the field of inexpensive plastic radio frequency identification (RFID) tags as well as TFTs. By employing such methods, the cost of each RFID tag can be reduced to 1 cent or less because passivation processes and lithographic methods are not required. Furthermore, if the on-off ratio of printed TFT using the invented method could be improved up to 10², this method will be applied to construct macroelectronic devices such as e-paper, organic light emitting display, and disposable cellular phone.

We used an inexpensive commercially available inkjet printer (HP Deskjet 3845) to print TFTs containing SWNTs on 3M transparency film (CG3460) with precise control over the density and position. The major reason for using a commercial inkjet printer and flexible plastic films is to show how SWNTs are robust and give consistent values for printed devices under ambient conditions. A higher quality printer would permit finer structures.

This invention has advantages of very high mobility of 296 cm²/V·s with a transconductance of 49.3 μS which would not be attained using existing printing methods. Furthermore, TFTs printed using this method have stable electrical properties under ambient condition without any passivation because SWNTs do not need dopants to show desired electrical properties.

The underscoring novelty is in the use of SWNTs for both the electrodes and the active layers by simply taking the bulk SWNTs and either using them directly for the electrodes (but as soluble species in surfactant-wrapped form) or the ps-SWNTs which are enriched in semiconductors (metallics having been suppressed by functionalization) in alcohol- or water soluble forms (such as aryl sulfonic acids or arylicarboxylic acid functionalized SWNTs).

In terms of variations, the printed TFTs using the invented method can have two different structures such as top active layer or top source-drain structures. In addition, SWNT electrodes can be replaced by metals, and semiconductors as the active layer can be changed to conducting oligomers or polymers. Finally, while the discussion herein has focused on SWNTs, such methods could be modified to utilize other types of carbon nanotubes instead of, or in addition to, SWNTs. Suitable other types of carbon nanotubes include, but are not limited to, multi-wall carbon nanotubes, double-wall carbon nanotubes, small-diameter (<3 nm) carbon nanotubes, and combinations thereof. Also, wrapping nanotubes in nonionic surfactants, such as pluronic, can cause them to act as excellent inks in this process. Finally, Applicants have recently found that polyethylene glycol can be added to the SWNT inks to serve as an excellent co-additive for the uniform inking of substrates with pristine or functionalized SWNT solutions.

The following examples are included to demonstrate particular embodiments of the present invention. It should be appreciated by those of skill in the art that the methods disclosed in the examples that follow merely represent exemplary embodiments of the present invention. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments described and still obtain a like or similar result without departing from the spirit and scope of the present invention.

EXAMPLES

Example 1

SWNT TFT

This example illustrates TFT results wherein very high mobilities were obtained. The results contained in this example were reported in Appendix A of the priority documents, U.S. Provisional Application Ser. No. 60/739,666 U.S. Provisional Application Ser. No. 60/775,060. The aforementioned Appendix A is a reproduction of a manuscript pre-print. This manuscript preprint has not been published.

FIG. 1 shows a schematic of an exemplary process of fabricating SWNT TFTs using a commercial ink-jet printer
for the electrode and active layer printing. The electrodes are SWNT bundles of m-SWNTs and s-SWNTs. The active layer is made from ps-SWNTs obtained using functionalization procedures. Gate dielectric layers are coated on printed gate electrodes using a bar coater.

FIG. 1 shows a schematic of an exemplary process of fabricating SWNT TFTs using a commercial ink-jet printer for the electrode and active layer printing. FIG. 2 shows I-V characteristics of a printed all-SWNT-TFT. FIG. 3 shows the corresponding transfer characteristics at V_{DS} of ~20 V.

Example 2
Prophetic Example—RFID Tag

Regarding RFID tags, FIG. 4 illustrates the layout of an exemplary multi-component RFID tag, where one component is a modulator (5), the modulator comprising a ring oscillator, and another component is memory (4) (see, e.g., FIG. 6). In some embodiments, the ring oscillator is fabricated by printing layers, as shown in FIG. 5, where a layer of gates and associated wires, all of SWNT bundles, are printed on a substrate, as shown in Step (a); an insulating layer (e.g., PMMA) is deposited, as shown in Step (b); a source and drain layer, together with the associated wiring, all of bundled SWNTs, is put down (i.e., printed) on the insulating layer, as shown in Step (c); and an active layer is put down on the source and drain layer, wherein the active layer comprises functionalized SWNTs. These steps lead to the formation of 5-stage ring oscillator 200 comprising layered elements 201. Those of skill in the art will recognize that the other RFID tag components can be fabricated (i.e., printed) in similar fashion.

Example 3
SWNT-Diode

We have developed a SWNT-diode to construct a rectifier for providing DC power to a printed RFID tag. A SWNT-diode was prepared using the present printing method. First, an Au electrode was printed on a PET substrate using Au ink and an inkjet printer. On the printed Au electrode, PEDOT was printed on the pattern of printed Au. Selectively functionalized SWNT ink to knock out metallic SWNT was then printed on the PEDO patterns, and then finally a Ag electrode was printed on the SWNT patterns using Ag ink. The resulting SWNT-diode was characterized using a semiconductor analyzer. The characteristics of the SWNT-diode are shown in FIG. 7.

Example 4
Prophetic Example—Rectifier

The present inventors contemplate the following example. A conventional printed 13.56 MHz antenna is coupled to have 4 V AC, and then rectified using a SWNT-diode to give 2 V DC using a conventional rectifier circuit.

Example 5
Dielectric Polymer Wrapped SWNT

Using SDS stabilized SWNT solution, we just added monomer such as styrene and polymerized in situ using AIBN at 60°C. The resulting polystyrene (PS) wrapped SWNT could be used directly as active ink to print thin film transistor. A dielectric polymer wrapped SWNT is also described in Korean patent application No. 10-2006-0106023.

PS wrapped SWNT was characterized using TEM. 2 to 5 nm thick PS was coated on SWNT, as illustrated by the TEM image shown in FIG. 8.

All patents and publications referenced herein are hereby incorporated by reference. It will be understood that certain of the above-described structures, functions, and operations of the above-described embodiments are not necessary to practice the present invention and are included in the description simply for completeness of an exemplary embodiment or embodiments. In addition, it will be understood that specific structures, functions, and operations set forth in the above-described referenced patents and publications can be practiced in conjunction with the present invention, but they are not essential to its practice. It is therefore to be understood that the invention may be practiced otherwise than as specifically described without actually departing from the spirit and scope of the present invention as defined by the appended claims.

What is claimed is:
1. A process for making thin film (TF) electronic devices comprising the steps of:
   - using an ink jet printer mechanism to print electronic device patterns on a substrate as a composite ink mixture of metallic carbon nanotubes (m-NTs) and semiconductor carbon nanotubes (s-NTs), wherein the m-NTs are active and dominate the characteristics of the composite ink mixture in any of the electronic device patterns designated as a conductor patterns;
   - de-activating a portion of the m-NTs in any of the electronic device patterns designated as resistive device patterns;
   - de-activating substantially all of the m-NTs in any of the electronic patterns designated as semiconducting device patterns.
2. The process of claim 1, wherein de-activating the m-NTs comprises chemically reacting the m-NTs to inhibit or block their charge transport mechanism.
3. The process of claim 1, wherein the m-NTs in the electronic device patterns are de-activated in-situ.
4. The process of claim 1, further comprising the steps of:
   - drying an electronic device pattern forming a dried electronic device layer; and
   - washing the dried electronic device layer to remove any undesired residue.
5. The process of claim 4, wherein a layer of the composite ink mixture is applied with the ink jet mechanism over a dried electronic device layer to enhance a characteristic of one of the electronic device layers.
6. The process of claim 1 further comprising the step of applying a dielectric layer over one or more of the electronic device patterns.
7. The process of claim 6, wherein the composite ink mixture forming one of the electronic device patterns is applied over the dielectric layer.
8. The process of claim 6, wherein the dielectric layer is applied using a bar coating mechanism.
9. The process of claim 1, wherein the composite ink mixture of m-NTs and s-NTs is printed first to the electronic device pattern areas designated as the semiconductor device patterns.
10. The process of claim 1, wherein the m-NTs and s-NTs are selected from the set of carbon nanotubes consisting of single walled carbon nanotubes, multi-wall carbon nano-
tubes, double-wall carbon nanotubes, small-diameter carbon nanotubes, and any combinations of the aforementioned carbon nanotubes.

11. The process of claim 10, wherein a diameter of the small-diameter carbon nanotubes is less than 3 nanometers.

12. The process of claim 1, wherein the substrate comprises a flexible material selected from the set of materials consisting of polymers and papers.

13. The process of claim 1, wherein the conductor patterns, the resistive device patterns, and the semiconducting device patterns are un-passivated.

14. A thin film electronic circuit, comprising a circuit formed on a substrate to have a pre-determined functionality requiring conductors interconnecting a plurality of resistive devices, capacitive devices, inductive devices, and active semiconductor devices,

wherein the conductors, the resistive devices, the capacitive devices, the inductive devices, and the active semiconductor devices are formed at least in part by a process comprising:

using an ink jet printer mechanism to print electronic device patterns, on a substrate, as a composite ink mixture of metallic carbon nanotubes (m-NTs) and semiconductor carbon nanotubes (s-NTs),

wherein the m-NTs are active and dominate the characteristics of the composite ink mixture in any of the electronic device patterns designated as the conductors;

de-activating a portion of the m-NTs of the composite ink mixture in any of the electronic device patterns designated as the resistive devices; and

de-activating substantially all of the m-NTs of the composite ink mixture in any of the electronic patterns designated as a semiconducting portion of the active semiconductor devices.

15. The thin film electronic circuit of claim 14 further comprising the steps of:

applying a dielectric layer over an electronic device pattern after its m-NTs have been de-activated to a pre-determined level;

forming an electrode device pattern by printing the composite ink mixture over the dielectric layer; and

de-activating the electrode device pattern over the dielectric layer to form a conductor.

16. The thin film electronic circuit of claim 15, wherein the dielectric layer forms a gate region of a thin film transistor (TFT) and the electrode device pattern forms a gate electrode of the TFT.

17. The thin film electronic circuit of claim 15, wherein the dielectric layer forms a dielectric of a parallel plate capacitor and the electrode device pattern forms a plate of the parallel plate capacitor.

18. The thin film electronic circuit of claim 14, wherein a plurality of the active semiconductor devices are interconnected with the conductors to form at least part of logic circuitry and analog circuitry.

19. The thin film electronic circuit of claim 18, wherein the pre-determined functionality is selected from the group consisting of a radio frequency identification (RFID) tag, electronic paper (e-paper), an organic light emitting display, and a disposable cellular phone.

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