Print Fabrication and Characterization of CNT Transistors on Plastic Films

Hiroyuki Endoh

Smart Energy Research Laboratories, NEC Corporation
34, Miyukigaoka, Tsukuba, Ibaraki 305-8501, Japan
h-endoh@az.jp.nec.com

Keywords: carbon nanotube(CNT), thin film transistor(TFT), ink-jet printing

1. Introduction

Recently, printed electronics is expected to be a low-cost, eco-friendly, and on-demand fabrication technology because it decreases the number of process steps and the amount of waste materials. By using the printing method, the electronics devices should be able to manufacture at low temperatures, therefore the circuit can be fabricated directly into the plastic substrates. TFT semiconductor materials used to print has been well studied, the organic materials is reported mostly. However, there is a problem in the electrical characteristics of mobility of the TFT. In the case of the oxide semiconductor having a large mobility, is being developed to be applied to products such as large flat panel displays, but to apply to the plastic substrate has not been achieved, because of the high temperature processing is required.

As a new material for high-performance electronic devices, the carbon-based materials such as Fullerene, carbon nanotube (CNT) and graphene are expected. Single-wall CNTs[1] have a large intrinsic mobility[2] and are considered as a promising new electronic material. However, a crucial problem for the application of CNTs to electronics is that their electronic properties depend on the diameter and chirality, and thus, they intrinsically contain metallic (m-)CNT contamination[3]. According to simulation studies[4], a CNT random network[5] tolerates m-CNT contamination. In addition, CNT networks are solution process compatible, bendable, and can be treated in the atmosphere at a low process temperature; therefore, they are suitable for printed TFTs. A flexible and high-mobility TFT was fabricated using a solution-processed CNT network with an additional patterning process. It showed an excellent potentiality of the solution-processed CNT network channel[6]. Ink-jet printing is a promising candidate for direct patterning, and it has been adopted to fabricate CNT TFTs with evaporated Au electrodes.

2. Structure and characteristics of CNT

Single-wall CNT has a new form of carbon with unique electrical and mechanical properties. CNT is the material of hollow shape, as shown in Fig.1, is a straw-like structure was rounding a graphene sheet. In general, the diameter of the single-wall CNT is 0.7~2.0nm, and the length is 1~10um. Depending on the folding angle and the diameter, CNTs can be metallic or semiconducting. Simple theory also shows that the band gap of semiconducting CNTs decreases with increasing diameter.

Fig.1. Structure of single-wall CNT.
CNTs have a long one-dimensional structure, the strength of carbon-carbon bond is very strong, and therefore CNTs have excellent stability. TFT using the single-wall CNTs with the very large mobility has been reported[7]. However, it is difficult to fabricate a stable TFTs, because of single-wall CNTs contain m-CNTs. By using CNT networks for TFT channel, it is tolerated m-CNT contamination, but it is required the purification of the CNTs to achieve high performance of the TFTs.

3. Separation of Metallic and Semiconducting Single Walled Carbon Nanotubes

This section, we described a separation method of metallic and semiconducting SWCNTs. Unique separation phenomena, which metallic and semiconducting SWCNTs layer was finally constructed separately, were confirmed when the electric field was applied vertically into the SWCNTs solution dispersed by using polyoxyethylene stearyl ether (Brij 700, Aldrich) as a dispersant of nonionic surfactant. Because this separation is ionic-free process, simple procedure and equipment, it is applicable for mass production of separated SWCNTs for the industrial use such as electronic applications.

The dispersed SWCNT solution after controlling concentration of SWCNT and surfactant was introduced into the separation equipment. The separation equipment consists of a vertical cell with a pair of electrodes and a direct current (DC) power supply (ATTO, Cross Power 500). The cell is constructed by a polyvinyl chloride measuring cylinder with a 6-cm height and 2-cm diameter. A pair of looped-platinum wires is attached at the top and bottom of the cell with the distance of 5 cm as cathode and anode, respectively.

Fig. 2 shows the snapshot images in the operation of separating 1-nm diameter SWCNT at initial, after 4, 10 and 16 hours. During separation process, four types of unique different phenomenon were found in sequence. (1) First of all, brown particle was aggregated and then migrated toward the top side of the cell. At that time, single convection from the top to the bottom was confirmed in the cell. (2) After that, two colored regions were separated by horizontal interface constructed in the solution. The convections in each colored layer were separately constructed. (3) The separated layers are gradually thickened in each region. The individual convections in each layer were also confirmed. (4) Finally, the reddish layer and bluish layer were clearly formed at the top and bottom side, respectively. Because the condition of each layer became homogeneous, the convections of each layers were disappeared.

Fig. 3 shows the optical absorption spectra of upper-layer and lower-layer fractions of SWCNTs, together with the spectrum of starting source dispersion as a reference. The absorption peaks around 1.4–2.3 eV and 2.3–2.9 eV are derived from the second interband transition of semiconducting SWCNTs (S22)[8] and the first interband transitions of metallic SWCNTs (M11)[11], respectively. The spectrum shape in S22 and in M11 regions drastically changed before and after the operation. On the spectrum of the upper-layer fraction, the M11 peaks are enhanced against the starting dispersion of the pristine SWCNT sample and, in contrast, the S22 peaks are depressed. This result suggests the enrichment of metallic SWCNTs in the upper-layer sample. On the other hand, the opposite tendency was observed in the spectrum shape of the lower-layer fraction, that is, M11 peaks.
were extremely diminished while $S_{22}$ peaks were increased. It is remarkable that large $M_{11}$ peaks observed at 2.49 eV and 2.78 eV were almost completely disappeared in the spectrum of the lower-layer fraction, leaving small peaks with different positions.

4. Fabrication of CNT-TFT by ink-jet printing

Ink-jet printing is a promising candidate for direct patterning. We are using the CNT has been purified, was produced in the ink for ink-jet printing. CNT ink was prepared as shown in Fig.4.

<table>
<thead>
<tr>
<th>Water-based</th>
<th>Organic solvent-based</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent</td>
<td>Water</td>
</tr>
<tr>
<td>CNT</td>
<td>10 ppm</td>
</tr>
<tr>
<td>Surfactant</td>
<td>Dichloroethane (100 ppm)</td>
</tr>
<tr>
<td>Viscosity</td>
<td>2.8</td>
</tr>
<tr>
<td>Surface tension (mN/m)</td>
<td>42.5</td>
</tr>
<tr>
<td>Printing property</td>
<td>Good</td>
</tr>
</tbody>
</table>

Fig.4. Ink formulation for ink-jet printing.

CNT ink was prepared by mixing the solvent and CNT, and sonicate of about 2 to 6 hours, furthermore ultra-centrifugation. All CNT ink was shown very good dispersibility(Fig.5). In the case of using water solvent, it was necessary a surfactant.

We used ink-jet head system manufactured by Ricoh Corporation (E2-type). Ejection of CNT ink from the ink-jet head is in very good, clean circular droplet was observed in both water and organic solvents(Fig.6).

TFT substrates for printing the CNT is the following procedure, were prepared. First, gate electrodes using gold metal were deposited on polyimide films (Upilex-7S, Ube Industries) at a thickness of 100nm. Next, gate insulators were formed using spin coater with a polyimide ink (CT4112, Kyocera Chemical) and then cured. The thickness of the polyimide layer was 500nm. The leak current was less than $1 \times 10^{-13}$ A for a 40 V dc bias. Finally, source-drain electrodes were deposited on the gate insulator with gold metal at a thickness of 100nm.

In the case of using the organic solvent-based CNT ink, CNT pattern was not a clear, because of the wettability of the organic solvent ink to the polyimide film is very large(Fig.7). This is considered, because of spread the printing area rapidly before the drying. The mobility of this TFT is observed about 0.1cm²/Vs.

On the other hand, in the case of CNT water was used, printed pattern is very clear, and was able to obtain a uniform pattern printed line width about 60µm(Fig.8).
Transfer characteristics of the CNT TFTs measured with a gate voltage ($V_G$) of $-50 \text{V}$ to $+5 \text{V}$ at a drain voltage ($V_D$) of $-2 \text{V}$ are shown in Fig.9. The p-type behavior with an on/off ratio of 9,700 and a threshold voltage of $+3.4 \text{V}$ can be seen. It is considered, further improve the purity of the CNT and optimization of device structure, it can be further improved the performance of the printed CNT TFTs.

Fig.9. The transfer characteristics of the CNT TFT using water-based CNT ink by ink-jet printed.

5. Conclusion

As a new device fabrication method, we have discussed the development of CNT TFT manufacturing by inkjet printing process. For purification of the CNT, was successful in the separation of high purity semiconductor CNT in a very simple way. Currently, that can be fabricated by printing a TFT of the performance of almost the same as amorphous silicon or organic material. In particular, using the simple ink-jet printing method, we were able to fabricate high-performance TFT. It is showed the possibility of the TFTs fabricated by all printed process, including the gate insulator and the electrodes. It is considered, mobility of printed TFT achieve more than $10 \text{cm}^2/\text{Vs}$, it is possible to development printed RF-ID tags, printed memory, and printed LSI.

Acknowledgements

The author thanks Dr.Takao Someya, Dr.Tsuyoshi Sekitani for technical advice of ink-jet printing process. And the author also thanks Mr.Fumiyuki Nihey, Mr, Hideaki Numata and Dr. Shinichi Yorozu for useful discussions.

References