

Chemically-doped *n*-type carbon nanotube thin-film transistors: Doping concentration dependence and influence of ambient air

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Abstract

High mobility *n*-type carbon nanotube thin-film transistors are realized on a plastic film by a simple transfer process and solution-based chemical doping technique. The electron mobility is estimated to be 70 cm²/Vs with on/off ratio of 10⁵ in ambient air. The dependence of the device property on dopant concentration and the influence of ambient air on device performance are discussed.

1. Introduction

The networks of single-walled carbon nanotubes (CNTs) have attracted much attention as an active layer of thin-film transistors (TFTs). Such a thin-film material exhibits rather uniform property by averaging properties of individual CNTs, providing a route to practical uses of CNT-based electronic devices. The CNT-TFTs are expected to enable a fabrication of high-performance integrated circuits for flexible and transparent devices on a plastic film [1], using relatively simple, non-vacuum techniques such as solution, printing, and sheet transfer processes.

The control of the conduction type (p/n control) is an issue that must be addressed for the various CMOS based circuit applications. Techniques for p/n control have been proposed by utilizing chemical doping. However, the mobility of the *n*-type devices reported are still lower than those expected for CNT-TFTs, ranging from 1 to 10 cm²/Vs.

In this work, we report high-mobility *n*-type CNT-TFTs realized by transfer process and solution-based chemical doping technique. The dependence of device property on doping concentration and influence of ambient air on device performance are discussed.

2. CNT Growth and Device Fabrication

Growth of CNTs

CNTs were grown by an ambient-pressure floating-catalyst chemical vapor deposition (FC-CVD) technique with CO as the carbon source [2], wherein catalyst particles were produced by decomposition of ferrocene vapor. CO (50 sccm) was passed through a cartridge containing ferrocene powder. Additional CO (400 sccm) was introduced into the furnace. The growth temperature was 850°C. The CNTs were collected by filtering through a

membrane filter of cellulose acetate mixed with nitrocellulose at room temperature.

TFT fabrication based on transfer process

Bottom-gate TFTs were fabricated on a polyethylenenaphthalate (PEN) substrate. After forming of gate electrodes (Ti/Au: 10/100 nm) with conventional photolithography, electron-beam evaporation, and lift-off process, a 50-nm-thick Al₂O₃ insulator layer was deposited on the substrate by an atomic layer deposition technique using trimethylaluminum and H₂O at 145°C. Contact windows for the gate electrodes were then opened by photolithography and reactive ion etching. Then, a CNT film was transferred from a membrane filter to the substrate with the gate electrodes. Then, source and drain electrodes were formed by the same process as the gate. The CNTs outside the channel were removed by oxygen plasma. The channel length and width are both 100 μm.

We used polyethylenimine (PEI, MW 800) for electron donor as a previous report [3]. PEI was dissolved in methanol (0.01~20 vol%) and coated on devices by spincoating technique.

Figure 1 shows (a) a photograph of the devices fabricated on a PEN substrate and (b) a micrograph of a device and an SEM image of the channel. The density of CNTs was 0.1 μm⁻², which was about twice percolation threshold of 10-μm-long CNTs.

3. Results

Figure 2 shows *I*_D and *I*_G of fabricated CNT-TFTs with

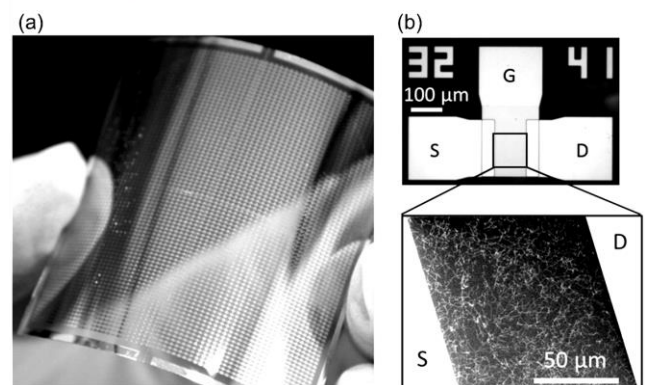


Fig. 1(a) photograph of array of CNT-TFTs fabricated on PEN substrate, and (b) microscopic photograph of a device and SEM image of the channel.

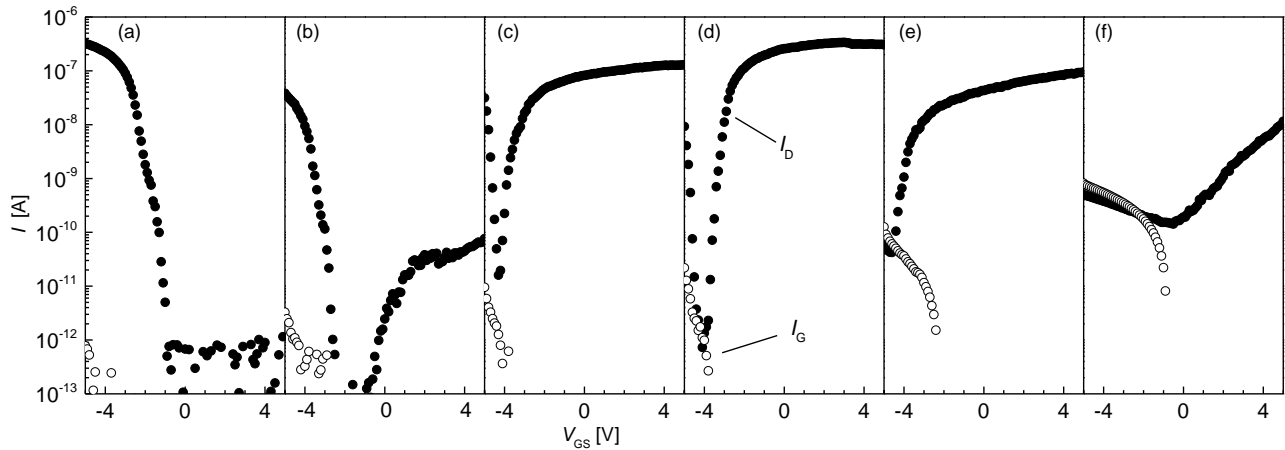


Fig. 2 I_D - V_{GS} (closed circle) and I_G - V_{GS} (open circle) characteristics of CNT-TFTs (a) without doping and (b) ~ (f) with doping. The PEI concentrations are (b) 0.01, (c) 0.1, (d) 5, (e) 10, and (f) 20 vol%. $|V_{DS}| = 0.5$ V.

various doping concentrations as a function of V_{GS} . The device showed n -type conduction for PEI concentration above 0.1 vol%. The best performance was obtained at a PEI concentration of 5%; the mobility was $70 \text{ cm}^2/\text{Vs}$ for rigorous gate capacitance model [4] and the on/off ratio was $\sim 10^5$. With further increase in PEI concentration, gate leakage current increased and then on/off ratio was degraded. The s -factor was also degraded with increasing PEI concentration. These phenomena would be due to the charges in the PEI layer.

Figure 3 shows the transfer characteristics of a n -type device measured in ambient air (broken line) and in vacuum (solid line). The p -type conduction was observed at negative gate voltage in air, i.e., so-called ambipolar conduction occurred. In addition, a large hysteresis was observed. In vacuum, on the other hand, the p -type conduction and hysteresis were suppressed. These results suggest that although the PEI has an ability to dope electrons to the CNTs in air, the surface passivation is necessary to protect the device from ambient oxygen and water that are considered to cause hole injection [5] and hysteresis [6] in carbon nanotube devices.

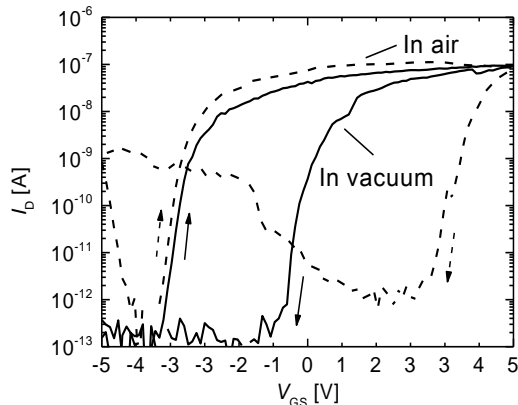


Fig. 3 I_D - V_{GS} characteristics of a CNT-TFT at $V_{DS} = 0.5$ V measured in ambient air (broken line) and in vacuum (solid line).

4. Conclusions

High-mobility n -type CNT-TFTs were realized on a plastic substrate by solution-based chemical doping technique. The high mobility CNT film was formed by the transfer technique based on FC-CVD technique. The electron mobility was evaluated to be $70 \text{ cm}^2/\text{Vs}$ with on/off ratio of $\sim 10^5$. Although ambipolar conduction and a large hysteresis were observed in ambient air, they were suppressed in vacuum.

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References

- [1] D.-M. Sun, M. Y. Timmermans, Y. Tian, A. G. Nasibulin, E. I. Kauppinen, S. Kishimoto, T. Mizutani, and Y. Ohno, *Nature Nanotech.* **6** (2011) 156.
- [2] A. Moisala, A. G. Nasibulin, D. P. Brown, H. Jiang, L. Khriachtchev, and E. I. Kauppinen, *Chem. Eng. Sci.* **61** (2006), 4393.
- [3] M. Shim, A. Javey, N. W. S. Kam, and H. J. Dai, *J. Am. Chem. Soc.* **123** (2001) 11512.
- [4] Q. Cao, H. S. Kim, N. Pimparkar, J. P. Kulkarni, C. J. Wang, M. Shim, K. Roy, M. A. Alam, and J. A. Rogers, *Nature* **454** (2008) 495.
- [5] S. Heinze, J. Tersoff, R. Martel, V. Derycke, J. Appenzeller, and Ph. Avouris, *Phys. Rev. Lett.* **89** (2002) 106801.
- [6] W. Kim, A. Javey, O. Vermesh, Q. Wang, Y. Li, and H. Dai, *Nano Lett.* **3** (2003) 193.