Printed Thin Film Transistors using Semi-conductive Single Wall Carbon Nanotube-Polymer Complexes

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ABSTRACT

We have achieved high performance on printed TFTs with a mobility up to 155 cm^2/Vs, which is world leading level performance as a printed TFT, using highly enriched semi-conducive single wall carbon nanotube (SWCNT) and semi-conductive polymer complexes. This technology can be applied to various IoT devices.

1 INTRODUCTION

Single wall carbon nanotubes (SWCNTs) have gained attention as a semi-conductive material for low-cost, flexible thin film transistors (TFTs) [1, 2]. One of the Key technology to fabricate CNT-based devices by low-cost printing process is how to make high-quality CNT inks. We have developed a technology to make a stable and uniform dispersion of SWCNTs by forming CNT and semi-conductive polymer complexes as shown in Fig. 1 [3, 4]. Excellent TFT devices can be fabricated by a common printing technology, such as an ink-jet, using the CNT dispersion. Recently, highly purified semi-conductive CNTs can be obtained by various separation methods [5, 6] and the electrical properties of CNT-TFTs have been dramatically enhanced.

In this work, high performance printed CNT-TFTs with a mobility up to 155 cm^2/Vs by precise control of CNT nanostructures, realizing CNTs with longer and smaller diameter distribution are reported. This mobility is higher than that of IGZO-based TFTs which are used in high end LCD displays and OLED displays, suggesting the applicability of the CNT-TFTs to various IoT devices such as disposal ICs and sensors. The performance of some simple circuits with a combination of both p- and n-type CNT-TFTs are also introduced.

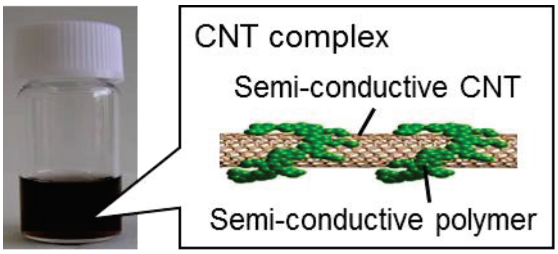

Fig. 1 Schematic image of a CNT complex

2 CNT NANOSTRUCTURE CONTROL

SWCNTs are synthesized as a mixture of metallic nanotubes (33%) and semi-conductive nanotubes (67%) and an individual semi-conductive CNT has extremely high electronic properties with a mobility over 10,000 cm2/Vs. Considering a practical use in mass production, a CNT network form is a better candidate because simple and low cost printing processes, such as an ink-jet printing, can be applied. However the high resistance at CNT junctions in the networks leads to a much lower mobility of network CNTs compared to that of an individual CNT. In order to get TFTs with high performance, metallic nanotubes has to be removed, and nanostructure of CNTs should be well controlled. Among the various technology to selectively gain semi-conductive CNTs, we introduced a gel column chromatography method developed by Kataura group [7], which enables us to obtain highly purified (>95%) SWCNTs. We also tried various CNTs with different synthetic methods and dispersion conditions. Consequently, we have succeeded in gathering CNTs with longer (>0.5 nm) and narrower diameter distribution (<0.2 nm). Furthermore, the crystallinity of CNTs is also improved.

As the CNT's quality increases, the uniform dispersion and the metal/semi-conductor separation become much more difficult. We found the pH control of the dispersion solution was very effective to increase the CNT dispersion ability without degradation of the CNT crystallinity. Furthermore the pH control also improved the separation ability. The absorption spectra of the CNT dispersion before and after adoption of the pH control are shown in Fig. 2. From the absorption area of semi-conductive CNTs, S_{22}, and metallic CNTs, M_{11}, we calculated S_{22}/M_{11} which exhibits the purity of semi-conductive CNTs. The S_{22}/M_{11} of 13.3 was obtained by the improved method, which is roughly double of that without the pH control. The high quality SWCNTs thus obtained were then formed complexes with a semi-conductive polymer in an organic solvent. The CNT inks prepared in this manner are uniform and highly stable.

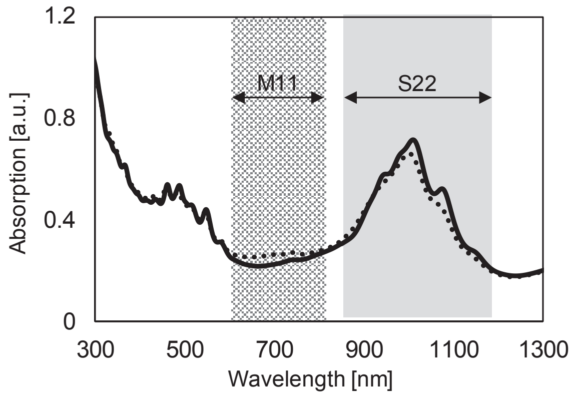

Fig. 2 Absorption spectra of the semi-conductor enriched CNT dispersions with (solid line) and without (dashed line) pH control in the separation process

3 TFT FABRICATION

We fabricated TFT devices with a bottom gate structure as shown in Fig. 3. A polymer solution was deposited as a gate dielectric layer on a glass substrate with a patterned aluminum gate electrode. Gold was then thermally evaporated and patterned to form source and drain electrodes with channel length (L) and width (W) of 10 μm and 10 μm, respectively. The CNT ink was ink-jet printed on the channel region to form a semi-conductive layer which consists of uniform CNT networks. All processes were conducted at 150°C or below.

Fig. 4 shows an AFM image of the ink-jet printed CNT networks. The CNTs form uniform networks and almost no bundles were observed.

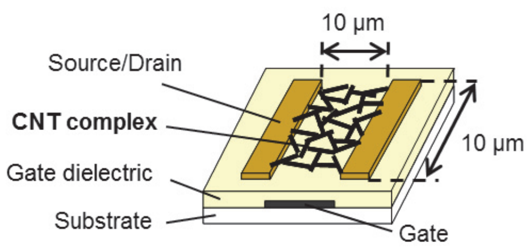

Fig. 3 Bottom gate TFT geometry using CNT complexes.

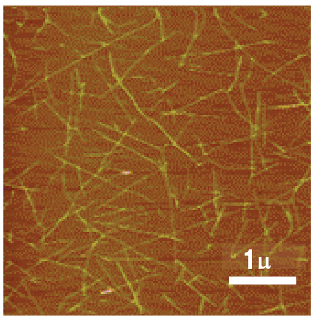

Fig.4 AFM image of the ink-jet printed CNT networks

The transfer characteristics were measured at a drain to source voltage of -5V as shown in Fig. 5. A normally-on property was observed as is generally seen in CNT-TFT devices. The printed device exhibited a mobility of 155 cm^2/Vs with an on/off current ratio of 10^6, which is world leading level performance as a printed TFT.

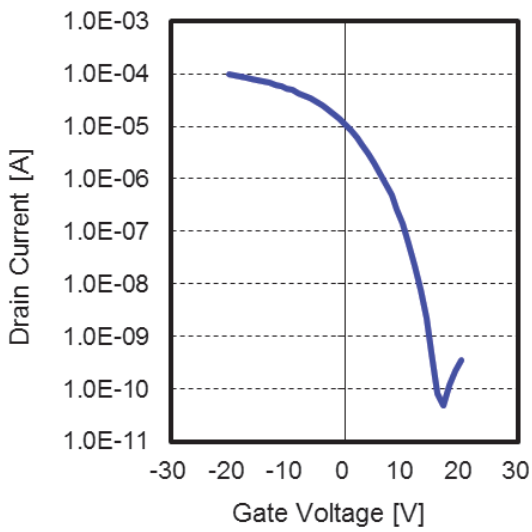

Fig. 5 Typical transfer characteristic of a CNT-TFT

4 CIRCUIT EVALUATION

As prepared SWCNTs possess p-type charge carriers because of positive doping caused by oxygen. Since the n-type TFTs are required for some applications, such as CMOS circuits, n-type CNT-TFTs have been extensively studied [7]. One of the promising approaches is incorporating an over-coating layer containing electron-donating chemicals onto the CNT networks. Although the n-type CNT-TFT properties have been dramatically improved, the ambient stability is still a big challenge. We have been successfully developed a new electron-donating over-coating material and evaluated the device stability. As shown in Fig. 6, the n-type TFT is stable in a humid condition (23°C, 70%RH) over several months, which enables us to apply CNT-TFTs to various CMOS applications.

By combining this new n-type CNT-TFTs with the p-type CNT-TFTs, we fabricated various circuit devices and evaluated their performance. For example, Fig. 7a shows a circuit diagram of a 21-stage ring oscillator. The outputs of the ring oscillator was measured at Vdd = 5V and the output waveform is showed in Fig 7b (top). The ring oscillator operated at an oscillation frequency of 19.8 kHz. Then we fabricated a D flip-flop connected with the 21-stage ring oscillator. The outputs of D flip-flop are also showed in Fig 7b (bottom). The D flip-flop operated at an oscillation frequency of 9.9 kHz, which is a half of that of the ring oscillator, suggesting these printed circuits are operated as designed.

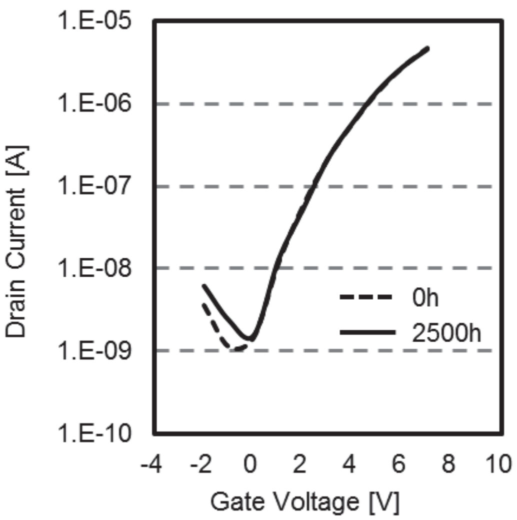

Fig. 6 Transfer characteristics of n-type TFTs before and after storing at 23°C, 70%RH

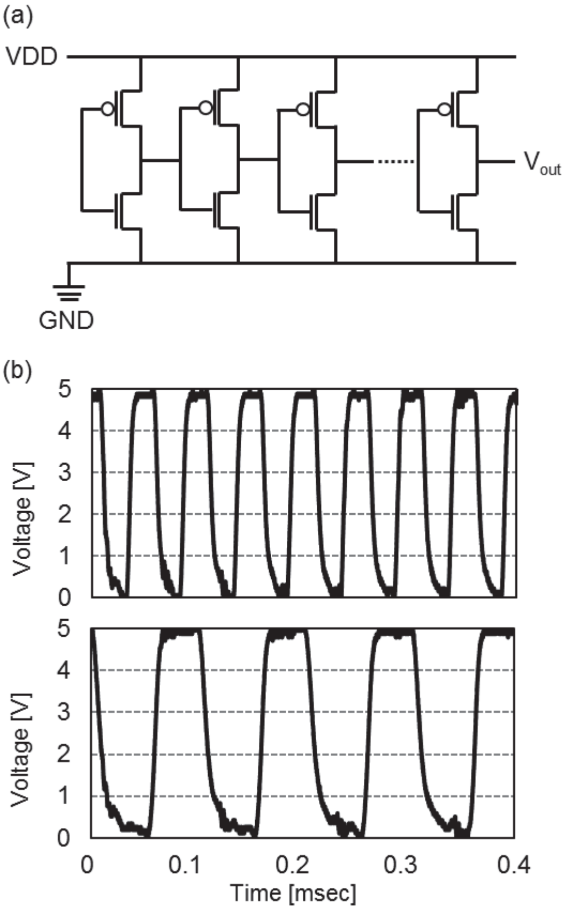

Fig. 7 (a) Circuit diagram of a 21-stage ring oscillator and (b) waveform of the 21-stage ring oscillator (top) and a D flip-flop (bottom)

5 CONCLUSION

We have developed high performance printed CNT-TFTs with a mobility of 155 cm^2/Vs by using nanostructure-controlled semi-conductive CNTs. A new over-coating material was incorporated on top of CNT networks to achieve high performance and stable n-type TFTs. By combining both p- and n-type CNT-TFTs, we succeeded in operating printed circuits. The CNT-TFTs can be fabricated by cost-effective role-to-role printing processes, which expect us to realize ultra-low cost printed circuits.

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