Extended Abstracts of the 2018 International Conference on Solid State Devices and Materials, Tokyo, 2018, pp627-628

SSDM2018
Fully-Printed Non-volatile Organic Thin-film Transistor Memory With DNA-Complex As A Gate Dielectric

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Abstract

Here, we demonstrate the utilization of an insulating biomacromolecule of DNA in the printed transistor memory. A new DNA derivative was synthesized *via* an ion-exchange reaction in the aqueous solution. Homogeneous molecular orientation in DNA derivative was achieved through a solution process in butanol, which can be employed as the dielectric with a densely packed structure and a good insulating property. The engineered DNA derivative enables to fabricate integrated organic thin-film transistor (OTFT) memories on a large-area flexible substrate in ambient atmosphere. Combining the results of low-frequency dependence of capacitance and a retention time of more than 100 seconds, this solution-processed DNA-complex was revealed to be a ferroelectric-like dielectric. The printed memories exhibit hole mobility of 0.65 $cm^2V^{-1}s^{-1}$ and a large memory window up to 13 V, which is enough for a plenty of applications. Therefore, this approach is promising for printing large-scale flexible OTFT memories and for realizing various integrated electronics.

1. Introduction

Non-volatile memory devices based on the organic thin film transistors (OTFTs) have been paid intensive attentions due to their solution processing approaches. Generally, non-volatile memories based on OTFTs are generally divided into three categories, i.e. ferroelectric, floating-gate, and polymer electrets-based ones. Among them, ferroelectric devices involve the polarization of gate dielectric, whereas the other two types mainly employ the charge storage ability. Most of ferroelectric polymers such as poly (vinylidene fluoride) (PVDF), its copolymers with trifluoroethylene (TrFE), nylons, and polypeptides, have been explored as the dielectric in OTFT memories. As ferroelectric polymers are soluble, solution-processing memory devices exhibit potential to realize “roll-to-roll” printing of light-weight, wearable electronic devices. However, the organic solvents to dissolve ferroelectric indeed dissolve many soluble organic semiconductors, making it difficult to achieve the layer-by-layer stacking structure in solution-processed organic TFT memories. Instead, organic layers are always thermally deposited or annealed in a high vacuum condition. Hence, suitable materials with ferroelectric properties, showing good solubility in common solvents without causing the erosion in organic semiconductors, are highly expected for the layer-by-layer integration of OTFT-based memory by printing techniques.

The biopolymer of DNA (deoxyribonucleic acid, widely available from salmon milt) and its derivatives exhibit a tunable insulating behaviour with dielectric relaxation. One of the DNA derivatives, DNA-CTMA (CTMA, hexadecyltrimethylammonium chloride), was already applied as dielectric in OTFT memory. Comparing with other ferroelectric polymer, DNA compounds prefer to dissolve in polar solvents, like water and alcohols, which are commonly treated as non-solvents for organic semiconductors. However, it revealed that DNAs suffer from a high leak current as the dielectric layer due to a large amount of mobile ions, which may become more serious when used in solution-processed electronics. Therefore, engineering the DNA molecule itself and its film configuration is essential, especially to enable printing multilayer electronics in ambient atmosphere.

2. General Instructions

The preparation of DNA-OTMA complex was performed by modifying the previously described methods as illustrated in **Figure 1a**. The ion-exchange reaction takes place between DNA and the surfactant complex (octadecyltrimethylammonium chloride, $OTMA^+$-Cl^-) and this process was carried out in the aqueous condition under ambient atmosphere. Eventually, the yield exceeds 60% and

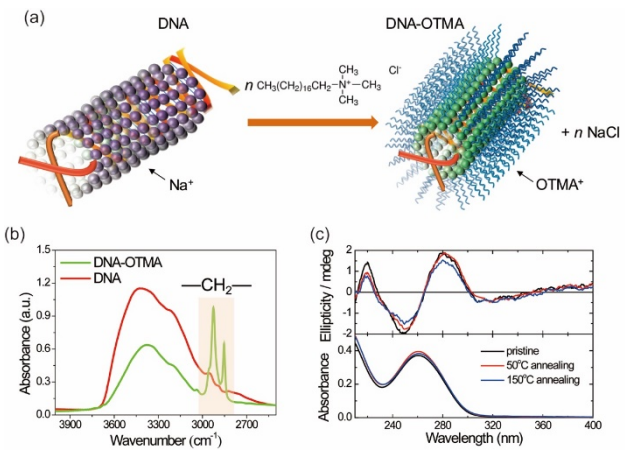

Fig. 1 (a) Schematic illustrations of the preparation route for DNA-OTMA complex. (b) Fourier Transform Infrared (FTIR) spectroscopy of DNA and DNA-OTMA. (c) Circular Dichroism (CD) and UV absorption spectra of pristine or annealed DNA-OTMA films.

could be further optimized for the mass production of such a biomaterial. The resulting DNA-complex solid was then placed in a vacuum oven at 50℃ for 24 hours for completely removing the residual water so as to ensure a good electrical property in the subsequent measurements.

To investigate the morphological structure of DNA-OTMA complex, a thin film was deposited on a silicon wafer by the simple spin-coating. Out-of-plane X-ray diffraction (WAXD) was performed to determine the long-range arrangement of DNA-OTMA chains. A sharp diffraction peak can be observed in the small-angle region and the *d*-spacing (*D*) is calculated to be about 3.9 nm, which could be corresponds to the diameter of the crystalline DNA-OTMA complex structure. Besides, a broad peak also appears covering a wide range of angles. The corresponding *d*-spacing value (*d*) of about 0.4 nm suggests the distance of the based pairs in the DNA-OTMA molecule. The diffraction density of X-ray at small angle region is rather higher than that at wide angle region. This result is typically observed in the planar molecular alignment in the DNA-OTMA thin film. Furthermore, the surface profile was investigated by atomic force microscope (AFM) images (2 μm× 2 μm), which reveals a rather smooth film by showing the root mean square (RMS) roughness of 0.354 nm. Even after a high temperature annealing, it still shows quite smooth surface confirming the thermal stability in aligned DNA-OTMA thin film. Moreover, such a small variation in the film thickness supports that DNA-OTMA molecules have homogeneously structure in the film, which is consistent with the observations in other DNA derivatives when using BuOH as the coating solvent.

The DNA-OTMA complex was then employed as the gate dielectric in printed OTFT memory devices as shown in **Fig. 2**. The devices are in the bottom-contact, top-gate configuration. On a 125 μm-thick plastic substrate (poly (ethylene 2, 6-naphthalate), PEN), a planarity layer of parylene-C (500 nm) was formed using chemical vapor deposition. The parylene-C surface was selectively exposed by the UV irradiations via a shadow mask to form hydrophilic patterns and then solution of Au nanoparticles

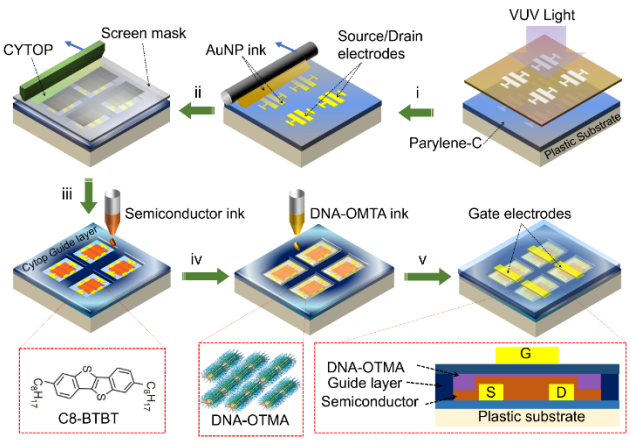

Fig. 2 Schematic illustration of fabricating printed OTFT memory array.

was sheared to print source and drain electrodes (**Fig. 2**, i). Then, the CYTOP (Asahi Glass) solution was screen-printed to form guide layers to direct the location of the organic semiconductors (**Fig. 2**, ii). Subsequently, the organic semiconductor dioctylbenzothieno- benzothiophene (C_8-BTBT, Nippon Kayaku) in a mixture of anisole and DMF solution was drop-casted onto the substrate and self-assembled into the bank areas surrounded by the guide layer CYTOP (**Fig. 2**, iii). After the solution was dried in air and the C_8-BTBT crystalline film arrays were formed. The dielectric layer was then fabricated by directly depositing the solution of DNA-OTMA in butanol on the top of C_8-BTBT thin films followed by spin-coating (**Fig. 2**, iv). The thickness of the dielectric film was controlled by adjusting the solution concentrations (See Figure S2 in Supporting Information). On DNA-OTMA, another thin layer of parylene-C was deposited as a protection layer to form a hydrophobic surface and finally Au top-gate electrodes were printed, using the same method as used in printing source and drain electrodes (**Fig. 2**, v).

The array of printed device on a flexible substrate was shown in **Fig. 3a**. The performance regarding of transfer and output characteristics are displayed in **Fig. 3b** and **3c**, respectively. The typical parameter of memory window can be extracted from the transfer curve and the largest value is estimated to be 13 V (from -5 V to 8 V). This value is comparable with that of the OTFT memory with the vacuum based PVDF-TrFE ferroelectric layer.

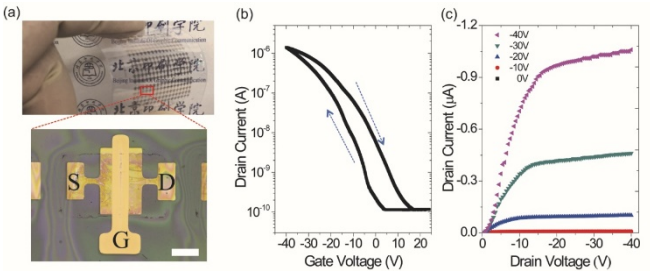

Fig. 3 (a) Images of DNA-OTMA based memory device on a flexible and transparent substrate; (b) and (c) Transfer and output characteristics of OTFT memory based the DNA-OTMA dielectric.

3. Conclusions

The presented proposed strategy will be promising for the achievement of roll-to-roll manufacturing of large-area, low-cost flexible electronic devices with ambient atmosphere.

References

[1]T.Minari*, Y. Kanehara, C. Liu, K. Sakamoto, T. Yasuda , A. Yaguchi, S. Tskada, K. Kashizaki, M. Kanehara*, *Adv. Funct. Mater.*, 24 (2014), 4886

[2] X. Liu, C. Liu, K. Sakamoto, T. Yasuda, P. Xiong, L. Liang, T. Yang, M. Kanehara, J. Takeya, T. Minari*. *NPG Asia Mater.*, 9 (2017), e409.

[3] L. Liang, X. Liu*, M. Kanehara, N. Kobayashi, T. Minari*. *Org. Electron.*, 55 (2018), 75.