Organic Electronics 55 (2018) 75–81

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Layer-by-layer printing non-volatile organic thin-film transistor memory with a planarly-oriented DNA-complex dielectric

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ARTICLE INFO

Keywords:
DNA
Non-volatile
OTFT memory

ABSTRACT

Printing device arrays of the non-volatile memory transistors is highly desired in the roll-to-roll manufacturing of integrated circuits. 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 s, 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 [1], floating-gate [2], and polymer electrets-based [3] ones. Among them, ferroelectric devices involve the polarization of gate dielectric, whereas the other two types mainly employ the charge storage ability. In principle, the ferroelectric field effect originates from the modulation of the surface potential of a semiconductor by the spontaneous polarization of a ferroelectric with electric field. In the ferroelectric-based OTFT memory device, the information to be stored is written by polarizing the gate insulator with a gate voltage pulse, and read out by controlling the channel conductance with a channel voltage pulse.

Most of ferroelectric polymers such as poly (vinylidene fluoride) (PVDF), its copolymers with trifluoroethylene (TrFE) [4–6], nylons [7], and polypeptides [8], 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 [9]. 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 [10]. 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

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https://doi.org/10.1016/j.orgel.2018.01.008
Received 21 December 2017; Received in revised form 4 January 2018; Accepted 13 January 2018
Available online 31 January 2018

applied as dielectric in OTFT memory [11]. 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 was also revealed that such 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.

In this study, we engineered the DNA molecules by attaching a long alkyl chain of OTMA (octadecyltrimethylammonium), obtained the planar molecular orientation in films, and then demonstrate printed OTFT memory based on DNA-OTMA. The long side chains and the planar orientation were found to be highly effective in decreasing the leak current and thus to enhance device performance. By controlling the assembly of DNA complex to form a uniform film, the OTFT memory devices exhibit hole mobility as high as 0.65 $cm^2 V^{-1}s^{-1}$ with memory window and retention time over 13 V and 100 s, respectively. Such approaches will provide a facile method for manufacturing biocompatible memory devices by roll-to-roll printing techniques in a large scale.

2. Results and discussion

We investigate the DNA-aliphatic surfactant complexes mainly because they are insoluble or poorly soluble in many polar solvents (e.g. water, acetonitrile, ethylacetate, etc.), but can be well dissolved in less polar solvent such as butanol. Such a feature enables the solution-processed deposition of thin DNA complex film (in several tens of nanometers) by the layer-by-layer assembly without erosion of the underlying organic layers. Besides, introducing alkyl chains into DNA molecules could increase the intermolecular distance for tunnelling of charge carriers, thus effectively enhancing the insulating property in the DNA-based thin films. The preparation of DNA-OTMA complex was performed by modifying the previously described methods [12] as illustrated in Fig. 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 (see Method in Supplementary Information). Eventually, the yield exceeds 60% and 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 °C for 24 h for completely removing the residual water so as to ensure a good electrical property in the subsequent measurements.

The structure of the obtained DNA-OTMA was characterized by Fourier transform infrared (FTIR) spectroscopy as shown in Fig. 1b. The absorption bands at 2861 cm^{-1} and 2955 cm^{-1} are assigned to the C-H stretching of CH_2 and CH_3 group and clearly indicate the OTMA groups have been successfully attached to the DNA chains to form DNA-OTMA complex, through the ion-exchange reaction between DNA and OTMA-Cl. Also, the characteristic absorption peaks from the C-O in sugar, sugar ring, and C=C ring can be found at 1062 cm^{-1}, 1010 cm^{-1} and 1606 cm^{-1}, respectively (see Fig. S1 in Supplementary Information), which support that the unique double helix structure of DNA has been maintained after the ion exchange-reaction. Furthermore, the FTIR shows the signals from the dipole groups with strong polarity including C=N ring (at 1575 cm^{-1}), C6=O (G), C2=O (C), and C4=O (T) groups (around 1660 cm^{-1}). In addition, the thermal stability of DNA-OTMA complex was investigated by the thermogravimetry analysis (TGA) in nitrogen atmosphere. Upon heating process, the DNA-OTMA complex film remains stable even at 240 °C, which can be comparable with pristine DNA salt. With such heat resistance, DNA-OTMA is expected to be applicable for the practical electronic devices.

In addition, temperature-dependent UV/Vis absorption and Circular Dichroism (CD) spectra of DNA-OTMA complex film were collected in Fig. 1c. From the CD spectra, the negative Cotton effect appears around 252 nm, while positive ones are observed around 220 nm and 282 nm. The observation is consistent with that in the natural DNA film [13].

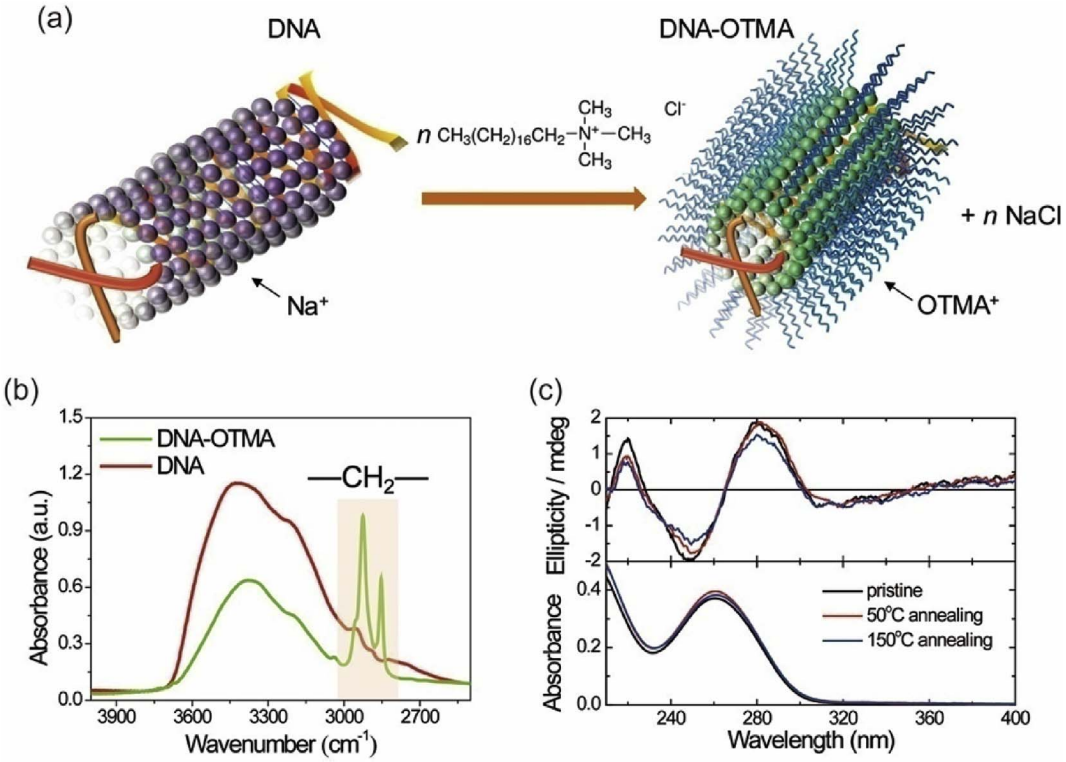

Fig. 1. (a) Schematic illustrations of the preparation route for DNA-OTMA complex. The molar ratio between DNA-Na and OTMA-Cl is 1:1.2. (b) Fourier Transform Infrared (FTIR) spectroscopy of DNA and DNA-OTMA. The characteristic peaks for methylene/methyl groups are highlighted at the wave numbers of 2860 and 2920 cm^{-1}, confirming the successful introduction of OTMA groups into DNA molecules. (c) Circular Dichroism (CD) and UV absorption spectra of pristine or annealed DNA-OTMA films.