High Temperature Hysteresis in Bio-Organic Field-Effect Transistor based on DNA-CTMA as Gate Dielectric

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Recently, DNA-CTMA lipid complex as the environmentally-friendly materials has been investigated extensively in novel functional optical and electronic devices. We have previously reported that the hysteresis mechanism of the nonvolatile transistor memory device in lower temperature region from -150 ~ -20 °C (L. Liang et al. Organic Electronics 28, 2016, 294-298). In this study, the hysteresis mechanism in the high temperature region range from 25 ~ 150 °C has been investigated through studying the temperature dependence of transfer characteristics, X-ray diffraction patterns (XRD), differential scanning calorimetry (DSC) as well as the dielectric performance of DNA-CTMA complex. The result indicates that the dipoles inside the DNA-CTMA stacking crystalline structure contribute to the appearance of hysteresis in bio-OTFT device at the high temperature.

Keywords: Nonvolatile transistor memory, DNA-CTMA lipid complex, Quasi-ferroelectric polarization

1. Introduction

Memory function is a prerequisite for many applications of envisioned electronic devices such as the memory card, radio frequency identification tag, e-signage and sensor [1,2]. In recent years, the non-volatile transistor memory array has been investigated extensively because it can maintain the stored data even when the electrical power supply has been turned off, and the inexpensive polymer materials [3-7] applied in the device are compatible with solution process such as printing, spin-coating and even spry coating on plastic substrates to achieve low cost requirement [8]. In addition, apart from these polymer materials, organic nonvolatile transistor memory devices need to develop the biodegradable, biocompatible, bioresorbable, or even metabolizable products as the components [9]. It is because that with the economic growth and the increased use of plastic electronic, the plastic waste problem may also increase dramatically, especially in the developing countries [10]. In our previous study, we have reported the biopolymers such as polypeptide worked as the gate dielectric layer of OTFT memory device [11-13].

DNA, one of the famous biopolymer, is a unique three-dimensional molecule with the sequence of four base pairs, plays an important role for all livings. And DNA is negatively charged polyelectrolyte, the negative charge always compensated by inorganic cations such as sodium ions [14], so the purified DNA is soluble only in water. In order to improve the solubility in organic solvents and the mechanical strength of the DNA film, Tanaka et al. [15] first made use of cationic surfactant in the preparation of DNA lipid complex. After this novel finding, many researchers began to utilize the DNA surfactant complex for the application in electronic devices, including organic light emitting diodes, quantum dots and organic thin film transistors as well as solar cells. And the
Performance of the BioTFT memory has been improved through applying various DNA lipid complexes and their derivatives. However, the memory mechanism still contradicted although tremendous progress has been made [16,17], in the previous study, we have investigated the hysteresis mechanism of the BioTFT through studying the electronic performance in the lower temperature region. However, the mechanism still not clear at the room temperature even in the high temperature.

In this study, we demonstrated a top contacted non-volatile transistor memory with DNA-CTMA lipid complex and pentacene as a gate dielectric and semiconductor, respectively. In order to study the hysteresis mechanism, the temperature dependence of transfer characteristic and and XRD, differential scanning calorimetry (DSC) as well as the dielectric performance of DNA-CTMA complex have been investigated in the high temperature region range from 25 ~ 150 °C. It is clearly seen that the fabricated device exhibits the memory behavior. And the relationship between molecular structure of DNA-CTMA complex and hysteresis mechanism has been presented successfully.

2. Experimental

2.1. Materials

The sodium salts of DNA (bp = ca. 100) were provided by Prof. Ogata and Piotrek Co. Ltd. Pentacene (98% purity) was supplied by Naad Co., Ltd. CTMA (98% purity), Butanol and common chemicals were purchased from Tokyo Chemical Industry Co., Ltd.

2.2. Preparation of DNA-CTMA complex and the BioTFT memory device

The preparation of DNA and DNA-CTMA complex film were reported in the former study [17], and the film thickness of the DNA film and the DNA surfactant complex films were 2 μm, respectively.

BioTFT memory devices were also fabricated according to the former study [17]. The BioTFT structure using a top contact and gate bottom geometry is schematically depicted in Fig. 1 with the chemical structure of DNA and DNA-CTMA complex.

Fig. 1. Chemical structures of (a) DNA and (b) DNA-CTMA. (c) Schematic structure of OTFT memory, DNA and DNA-CTMA are used as gate dielectric layer.

2.3. Apparatus

Thermal properties of DNA derivatives were analyzed by the DSC analyzer, (Bruker, 3200 SA). All electric measurements were carried out using a Keithley 4200 semiconductor parameter analyzer under dark conditions in vacuo. The voltage scan rate in transfer property measurements at different temperatures was automatically controlled by a measurement program. Dielectric spectroscopy measurements were performed using an impedance analyzer (Solatron, SI1296).

![Fig. 2. Transfer characteristics of the OTFT with DNA-CTMA as gate dielectric at higher temperature region.](image-url)
3. Results and discussion

Figure 2 shows the transfer characteristics at higher temperature region ranging from 50 to 150 °C with the drain-source voltage (VDS) maintained at – 10 V. As shown in the figure, the stable and sizable hysteresis loops were well observed at each temperature, suggesting that the prepared memory device can be operated not only in the lower temperature region, but also in the high temperature region, this finding lay a solid foundation to certificate that this Bio-OTFT memory device can be operated in a wide temperature range. Further, the ON current at gate voltage of - 60 V and the OFF current at + 60 V increased simultaneously with increasing temperature. This can be explained by the positive temperature dependence of electrical conductivity in pentacene layer. And the ON/OFF current ratio at gate voltage of 0 V approached to the maximum when temperature increased to 100 °C, indicating the variation of carrier charges accumulated at the interface has changed with increasing temperature. In addition, as shown in Fig. 2, the turn-on voltage shifted positively with increasing temperature, indicating that the conformation of DNA-CTMA complex may change with temperature increasing.

Based on the above discussion, we carried out the DSC measurement to demonstrate the thermal performance of the DNA-CTMA complex film. Figure 3 shows the DSC curve of the DNA-CTMA complex under high temperature range from -20 to 120 °C on the heating runs, with the heating rate of 20 °C/min. In order to make the experimental result more reasonable, the DSC curve of pure DNA also is illustrated. As shown in the figure, a base shift at around 75 °C of both pure DNA and DNA-CTMA complex was observed, which was a critical temperature associated to the phase transition of double helix structure of DNA main chain. In our previous study, it has already been certificated that the DNA-CTMA complex maintained the same double helix structure as DNA itself after the ion exchange reaction. Above this phase transition temperature, the free volume of DNA-CTMA complex was also expected to increase, suggesting the conformation of DNA-CTMA complex changes above this phase transition temperature. From Fig. 2, at the temperature above 100 °C, the ON/OFF current ratio at gate bias of 0 V start to decrease with temperature increasing, supporting the results of DSC analysis very well. Therefore, the change of ON/OFF current can be attributed to the conformation change of the DNA-CTMA complex film. For the purpose of investigating the structure of the DNA complex at different temperatures, the temperature dependence of XRD spectrum was studied.

Figure 4 shows the XRD pattern in the Bragg reflection geometry of the DNA-CTMA complex film. The two primary peaks corresponding to the diameter of DNA-CTMA complex in the wide angle region and the distance of the alkyl chains in the small angle region were observed, respectively. As the temperature increase, there are systematic increases in the peak intensity of the XRD peaks, indicating that the molecules of DNA-CTMA complex present a more ordered state. In addition to the increasing intensity, there are also systematic shifts of the peak with temperature increasing. In the wide angle region, the peak shift to smaller 2θ values. Such a shift indicates an increase in the inter-planar spacing of alkyl chains of surfactant,
suggesting a possible alkyl chain lattice expansion or distortion in DNA-CTMA complex. On the contrary, in the small angle region, the peaks shift toward to the higher 2θ value of the diffraction angle, indicating that the DNA-CTMA stacking crystalline phase and/or stacked crystalline structure have been changed, namely, the lattice spacing decrease when the temperature above the phase transition, this can be attributed to the structural relaxation of the DNA main chains, which is consistent well with the DSC analysis in the higher temperature range (Fig. 3).

Fig. 5. The variation of the real part of the dielectric constant as a function of temperature at some frequencies for DNA-CTMA complex film.

Figure 5 shows the real part of the dielectric constant at the elevated temperature range from -150 to 150 °C. It can be seen from this figure that the real part of the dielectric constant decreases with increasing frequency. For instance, with increasing frequency from 20 Hz to 10k Hz, the step shifts from 0 °C to 75 °C. A similar relaxation process in other polymers such as nylons has been observed and attributed to the orientation of dipoles, which is controlled by the motions of large segments of the molecules [18]. In addition, the dielectric constant increase with increasing temperature. Therefore, from the temperature dependence of transfer characteristic in the high temperature range (Fig. 2), the ON/OFF current ratio at gate voltage of 0 V increased with increasing temperature in the range from 50 to 100 °C. However, it started to decrease when the temperature above the phase transition, it can be ascribed that after the phase transition temperature, because the variation of the crystal structure of the DNA double helix structure (Fig. 4), the DNA molecule begin to coil and the base pairs are inclined to twist, which can make the dipole moment of one strand cancels the other and decrease. Namely, above the phase transition temperature, the intense thermal motion of the DNA-CTMA molecules favored the disorientation and hindered the alignment of the dipoles along the electric field direction. Therefore, the accumulated charge carrier at the interface between pentacene and DNA-CTMA complex decreased and the hysteresis behavior exhibited the shrink shape. But the increasing magnitude of dielectric constant rise sharply with further increase in temperature, it was attributed to the charge carriers accumulating at interface between amorphous and crystalline regions within the bulk of DNA-CTMA complex (interfacial or MWS polarization) and/or at the interface between the DNA-CTMA complex and the electrodes (electrode or space charge polarization), that has different polarization mechanism with the bulk of the dielectric.

Fig. 6. Temperature dependence of the loss tangent for DNA-CTMA complex film.

Based on the observation of the dielectric loss tangent as a function of the temperature at a given frequency, the dielectric relaxation process can be illustrated more clearly. Figure 6 shows the temperature dependence of the dielectric loss tangent ranging from 0 °C to 150 °C at the fixed frequencies. As illustrated in the figure, as the temperature increase, the molecules absorb enough energy, thus giving the double helix main chain backbone enough kinetic energy to vibrate with the electric field frequency and the α relaxation peak can been obtained. Namely, the joint motions of the main double helix chain and existing dipoles give rise to the α peak. Further, with increasing electric frequency, the α relaxation peaks shift to the higher
temperature range, suggesting that under the rapid variation of the frequency of the electric field, higher temperature is needed for dipoles approaching the maximum degree of freedom. It is further verified that the polarization originated from the dipoles inside the DNA-CTMA complex was the main source of hysteresis.

4. Conclusion
The BioTFT memory device fabricated with DNA-CTMA complex as gate dielectric could work even at high temperature. And the temperature dependence of transfer characteristic, X-ray diffraction patterns, differential scanning calorimetry (DSC), and dielectric measurements indicated that the phase transition of 75 °C plays an important role in the hysteresis behavior of the BioTFT memory device. It is further verified that the quasi-ferroelectric polarization originating from the dipoles inside the DNA-CTMA complex is a possible source of hysteresis.

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