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論文題名（外国語の場合は、その和訳を併記）
Thesis Title（foreign language title must be accompanied by Japanese translation）

和題：DNA複合体を用いたOTFTメモリの構築とその動作機構解析
英題：Fabrication and Memory Mechanism of DNA-based Bio-Organic Field Effect Transistor Memory
In the last forty decades, conventional microelectronic devices have been made great progress with the development of the world. Since the first silicon transistor was produced, in a very short period of time, transistors replaced vacuum tubes in integrated circuits for the controlling appliances and machinery, the inorganic silicon and silicon dioxide insulators have been the backbone of the electronic industry. However, the limitations of rigid semiconductor wafers and higher cost of the silicon-based technique prevent the application of inorganic microelectronics in the large areas and on flexible substrates. Therefore, it is necessary for researchers to find and prepare more desirable materials to replace the inorganic materials.

Since Koezuka and his co-workers reported the first organic field–effect transistor (OFET) based on the polythiophene as the organic polymer semiconductor, a wide variety of organic materials have been developed and many devices performance related issues including carrier transport, contact resistance, carrier injection, surface treatment and gate dielectric materials have been investigated. Nowadays, organic electronics appeal to a broad range of products such as electronic memories, flexible displays, sensors as well as solar cells.

A memory function is a prerequisite for varieties of applications of electronic devices. The thin-film transistor (TFT) non-volatile memory (NVM) devices have been attracting great interest not only because of their low cost through the use of substrates such as plastic and paper, but also because of their solution processability by methods such as spin-coating, spray coating, or even inkjet printing. In the past few decades, organic thin-film transistors (OTFTs) have made remarkable progress as promising devices for the future development of applications such as radio frequency identification tags, removable storage devices, and chemical sensors.

Based on the first study on the effect of different polymeric insulators on carrier mobilities of organic semiconductor was reported, poly(vinylidene fluoride) and its copolymer with trifluoroethylene, P(VDF-TrFE), polyvinyl alcohol (PVA), certain kind of nylon, poly (methyl-methacrylate) (PMMA), and odd-numbered nylons have been applied as the gate dielectric materials extensively, the prototype of ferroelectric polymer memory has already been developed and the investigation for mass production is ongoing.

Apart from these polymer materials, organic thin film transistor memory devices need to develop the biodegradable, biocompatible, bioresorbable, or even metabolizable products as the components. It is because that with the economic growth and the increased use of plastic electronic, the plastic waste problem may also increased dramatically over the already forecasted enormous increase, and the plastic
consumption and waste have already been a major concerns in the world nowadays, especially in the developing countries. Therefore, the environmentally friendly electronics based on natural material is essential to be investigated. In this thesis, one of the most famous biopolymers, DNA, which comes from the salmon fish is employed as the gate dielectric material to fabricate the organic thin film transistor memory device.

DNA, one of the famous biopolymers, is a nucleic acid containing the genetic instruction on the sequence of the amino acids, the natured and purified DNA is soluble only in water. The resulting film are too water sensitive and have insufficient mechanical strength. Further, DNA is anionic polyelectrolyte which normally contains movable cations such as sodium ions. The water molecule and movable ions therefore lead to the poor device performance, which limit the application in the photonics and optoelectronics fields. However, the DNA lipid complex, which could be soluble in organic solvent and effective to reduce the movable counter ions such as sodium ions existing naturally in DNA through ion exchange reaction, have been made a wide application in electronic devices including OTFT memory. However, the detailed memory mechanism of DNA complex is rare and a complete picture of the physical background that may cause the hysteresis is still missing.

In this thesis, in order to prepare high quality thin films of DNA, different kinds of surfactants such as cetyltrimethylammonium chloride (CTMA) and octadecyltrimethylammonium chloride (OTMA) were applied to prepare the DNA complex, and the physicochemical performance of DNA complex has been investigated in Chapter 2 in detail. In addition, the different molecular weights DNA also have been studied to analyze the effect of DNA chain length on the physical properties of DNA complex. The physical performance mainly including resistivity, optical characteristics, surface morphology, thermal stability and micro-structure have been studied in detail based on many kinds of methods such as I-V characteristic analysis, IR, UV-vis, circular dichroism (CD), atomic force microscope (AFM) and X-ray diffraction spectra, respectively. In conclusion, I-V analysis suggested that the low molecular weight DNA showed the better resistivity than the high molecular weight DNA when the same surfactants were applied, and alkyl chains also have significant influence on the resistivity of DNA complexes. Circular dichroism (CD) analysis indicated that right-handed double helix structures of DNA complex (B-form) were retained in the film state, although the structure was A-form in the butanol solution. TG analysis suggested that the DNA complex shows the excellent thermal stability. AFM analysis indicated that the smoothness and the film formability of the complex of shorter DNA was higher than that of the complex of longer DNA complex extremely. The last but not
least, based on the XRD analysis, the diameter of DNA complex and distances of alkyl chains of surfactant have been confirmed.

Chapter 3 presents the fabrication of non-volatile transistor memory device. The DNA-OTMA and DNA-CTMA complex have been employed as the gate dielectric layer to prepare the BiOTFT memory device, respectively. For the purpose of obtaining the device with outstanding electronic performance, the effect of film thickness of dielectric and post annealing temperature on the transfer characteristics has been investigated. In addition, in order to obtain insights into the electric parameters, the morphology and crystal structure of semiconductor have also been studied in detail. Last but the least, the time-resolved measurement was also performed to estimate the retention time of the stored charges remaining in the DNA complex gate dielectric, namely, the storage time of the memory element, which is one of the most important parameters of memory device. According to results of the thickness dependence, it is indicated that with increase in the film thickness, the electronic parameters such as ON current decreased and the threshold voltage increased, thus leads to the shrinkage of the hysteresis loop. However, in order to guarantee the resistivity of the gate dielectric layer, the optimum film thickness of DNA complex was prepared as 2 μm. And the study of post annealing analysis demonstrated that post-annaling at elevated temperatures does not play a positive role in the improvement of the performance of the OTFT memory device. The possible reasons are that the higher post-annealing temperature could lead to the decrease of grain size of the pentacene film which has been deposited on this DNA complex film, resulting in less charge carriers accumulated at the conducting channel and larger threshold voltage. In addition, the switching performance and memory retention indicated that the stabilized driven BiOTFT based on DNA complex exhibited stable memory properties.

The cause of the hysteresis mechanism of BiOTFT memory device based on DNA complex as gate dielectric has been demonstrated in Chapter 4. Firstly, the memory mechanism of non-volatile transistor memory device based on the poly (γ-methyl-L-glutamate) PMLG as the gate dielectric has been investigated. PMLG, a synthetic polypeptide, has a highly ordered structure. In the case of PMLG thick films, a cholesteric-like structure was observed and the film exhibited ferroelectric behaviour without requiring any other special treatment such as poling, annealing, or stretching. In previous study, we reported the fabrication of an OTFT memory device using a thin PMLG film as a ferroelectric layer. And we also investigated the effect of the tertiary structure of PMLG molecules on the hysteresis of OTFT memory devices, i.e., memory performance. We found that the hysteresis of the OTFT memory device is strongly
affected by the helical tertiary structure of PMLG molecules, similar to the structure of a cholesteric liquid crystal phase. However, sufficient explanations about the memory mechanism using PMLG molecules have not yet been reported. Therefore, the same as the analysis method of DNA complex, first of all, the physicochemical characteristics of PMLG film have been investigated. In addition, the relationship between hysteresis behaviour of the memory device and chain motion of the PMLG molecule has been studied, which laid a solid foundation for investigating the memory mechanism of DNA based BiOTFT memory device. In summary, the physicochemical properties of Poly (γ-methyl-L-glutamate) (PMLG) such as Infrared spectroscopy (IR spectroscopy) and Circular dichroism (CD) spectroscopy has been studied in detail. And the pentacene based OTFT memory device with PMLG as gate dielectric has been fabricated. The electronic performance mainly including transfer characteristic and output characteristics at room temperature have been measured, and the ON/OFF current ratio, threshold voltage, carrier mobility have been extracted and calculated respectively. Further, the effect of annealing temperature on the electronic performance of polypeptide based OTFT memory device has been studied. In addition, the relationship between hysteresis behavior of the memory device and chain motion of the PMLG molecule has been investigated through evaluating the temperature dependence of the transfer characteristics, thermally stimulated depolarization current (TSDC) as well as differential scanning calorimetry (DSC). It was revealed that the cooperative movement of the large dipole moment along the rod-like main chain and that of the small dipole moment in the side chain played an important role in the memory function.

Taking example from the analytical methods of PMLG based OTFT memory device, the hysteresis mechanism of DNA complex based device is investigated successfully investigated through observing the same performance. In addition, the temperature dependence of capacitance-voltage (C-V) properties, dielectric behavior as well as the temperature dependence of XRD spectral has also been employed to confirm the explanation. In conclusion, the origination of hysteresis behavior of BiOTFT memory device with the temperature range from -150 °C to 150 °C has been put forwarded: the quasi-ferroelectric polarization originated from the alignment of intrinsic dipole moment inside the DNA-CTMA complex was thought to be the main source of hysteresis mechanism.

In summary, the DNA based BiOTFT memories has a potential to be a promising device for future development of varieties of applications such as smart tags, removable storage devices and chemical sensors.