공학석사 학위논문

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지도 교수 김 연 상

이 논문을 공학석사 학위논문으로 제출함

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이지현의 석사 학위논문을 인준함

2012년 8월

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Abstract

In this paper, we demonstrated non-volatile memory effect of redox proteins such as myoglobin, hemoglobin, and cytochrome *c*. Also, we introduced the fabrication of non-volatile organic field-effect transistor (OFET) memory utilizing myoglobin as a charge trapping element. Redox proteins are composed of a heme structure containing an iron atom, which have an effect on charge trapping and releasing via reversible redox reactions. Myoglobin charge trapping layer in OFET-based memory showed a considerable memory window, which depended proportionally on the concentrations of myoglobin solutions. We obtained the maximum memory window of ~20 V as well as good endurance properties in ambient conditions. Also, other redox proteins could be successfully applied to the memory device which showed a reliable memory window.

Keywords: non-volatile memory, organic field-effect transistor memory, charge trapping, redox proteins, heme structure

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layer using 0.5 mM myoglobin solution. The results were measured in ambient conditions at room temperature.

1. Introduction

1.1. Organic Electronics

Electronic devices have traditionally fabricated using inorganic materials, rigid substrates, and high-temperature manufacturing processes. In contrast, organic electronics become significant issues in the commercial industry because of the ability to fabricate on low-cost and flexible substrates such as glass, plastic or metal foils [1,2]. Extensive studies have been performed in scientific fields in order to fabricate various electronic devices using organic materials, including organic thin film transistor (OTFT), organic light-emitting device (OLED), organic photovoltaic cell (OPV) and organic non-volatile memory devices (ONVM) [3-8]. Although organic electronic devices have much less reliability and performance than these of the inorganic materials based electronics, many researchers have focused on the organic electronic devices because they hold great potential for realizing lightweight and large-area devices via simple and mild process conditions.

1.2. Memory Devices

Memory devices are crucial for storing information therefore they are regarded as important elements of a direct circuit in computers, mobile applications, and various electronic fields [9]. Metal-oxide-semiconductor (MOS) memories can be divided into two main categories: random access memories (RAM’s), which are volatile, i.e., they lose the stored data once the power supply is turned off, and read-only memories (ROM’s), which are non-volatile, i.e., they maintain the stored data also without power supply (See Figure 1) [10].

Typical types of volatile memories are dynamic random access memory (DRAM) which is composed of 1 transistor and 1 capacitor and static random access memory (SRAM). First, DRAM, which is the main memory system of computers, consumes relatively large power during refresh cycles. Nevertheless, it has been widely used because of rapid switching speed and low-cost. On the other hand, SRAM consists of 6 transistors per cell therefore it is faster and more reliable than the DRAM. But, the SRAM is relatively expensive and difficult to increase memory storage density [11].

A representative type of non-volatile memories is flash memory which is composed of 1 transistor per 1 cell and the stored information can be erased and reprogrammed in a block unit [11]. Figure 2 presents a comparison of non-volatile memory groups in terms of flexibility and cost. Flexibility indicates the possibility to be programmed and erased on many times in a system. Also, the cost is a direct function of the process complexity. Considering with the flexibility and cost, they show that flash memory offers the best compromise [10]. Non-volatile memory market share has been continuously growing in the past few years, and is forecasted to surpass DRAM market in the very near future [12]. For these reasons, we have interested in the non-volatile flash memory based on charge trapping effect.

1.3. Organic Field-Effect Transistor Memory

The developing of organic non-volatile memory (ONVM) devices with various functional materials is a rapidly emerging research field [13-15]. Among several types of organic memory devices, we have focused on the organic field-effect transistor (OFET) based memory, organic flash memory, which is an attractive issue because it is possible to fabricate simply and integrate directly the data storage sites within the memory device [16]. Figure 3 (a) and (b) show the structures of a conventional flash memory and the charge trapping OFET-based memory which have three layers: a control dielectric layer (blocking layer), a floating gate, and a tunnelling dielectric layer on the gate electrode. In OFET memories, the floating gate basically is defined as a charge trapping layer and the main function of the control dielectric is to prevent the leakage of charged carriers in the charge trapping layer. High energy is required to inject the charge carrieres over the tunneling barrier from the semiconductor channel into the charge trapping layer.The application of an external electric potential above a specific range results in the storage of charges in the trapping layer. These trapped charges alter the distribution of the charge carriers in the semiconductor channel [17]. This phenomenon induces the shifts of threshold voltage (V_{th}) of the transistor.

Consequently, V_{th} shift means the memory window of the non-volatile memory. For comprehending the memory operation, the energy band diagrams of the memory are schematically represented in Figure 4; the charged state and the uncharged state.

1.4. Redox Proteins

Redox proteins, which are also known as metalloproteins, have electrochemical properties since they have a redox active site such as a transition metal ion. These proteins are beginning to make significant attention in the bioelectric applications such as organic sensor devices and bio-memory because they can control a variety of biochemical reactions [18-20].

We introduced the representative types of the redox proteins as bio-functional materials in electronic application; myoglobin, hemoglobin and cytochrome *c*. These proteins have a heme structure, the non-protein active site, which is a prosthetic group consisting of a protoporphyrin ring and a central iron atom. Myoglobin is well-known as a monomeric heme protein, which is found mainly in skeletal muscles and carry out an intracellular storage site for oxygen. Hemoglobin is a tetrameric heme protein which is made up of four polypeptide chains. It is found in the red blood cells and is responsible for transporting oxygen from the lung to the tissue [21]. Cytochrome *c* is a small heme-containing protein acted as the electron transport chain in the mitochondria [22].

The iron ion in the heme structure can be either Fe^{2+} state or Fe^{3+} state.

In binding oxygen, Fe^{2+} is temporally oxidized to Fe^{3+} and Fe^{3+} is reduced to Fe^{2+} state when oxygen is released. Oxidation and reduction processes are reversible in redox proteins with the heme group. These properties serve wonderful opportunities for the heme-proteins in terms of various bioelectronics. Recently, various attempts have been made to use the redox proteins or enzymes in memory devices. For example, a flash memory with cobalt oxide (Co_3O_4) bio-nanodot (Co-BND) assembled by protein template was reported by Fuyuki et al [23]. However, the protein was used as only the template for ordering Co-BND, which was the direct memory element in the fabricated memory devices. Another example to fabricate memory devices based on bio-functional materials was a resistive switching memory (ReRAM) comprising polyelectrolyte/enzyme layer-by-layer (LbL) assembled multilayer as the memory active elements. But, the complicated and cumbersome processes of LbL assembly method of the polyelectrolyte/enzyme are required to organize the memory storage sites [24].

In this study, we focused on an effort to investigate the charge trapping effect of myoglobin in OFET-based memory device. That is, redox proteins could be a novel candidate as the charge trapping elements in non-volatile memory devices.

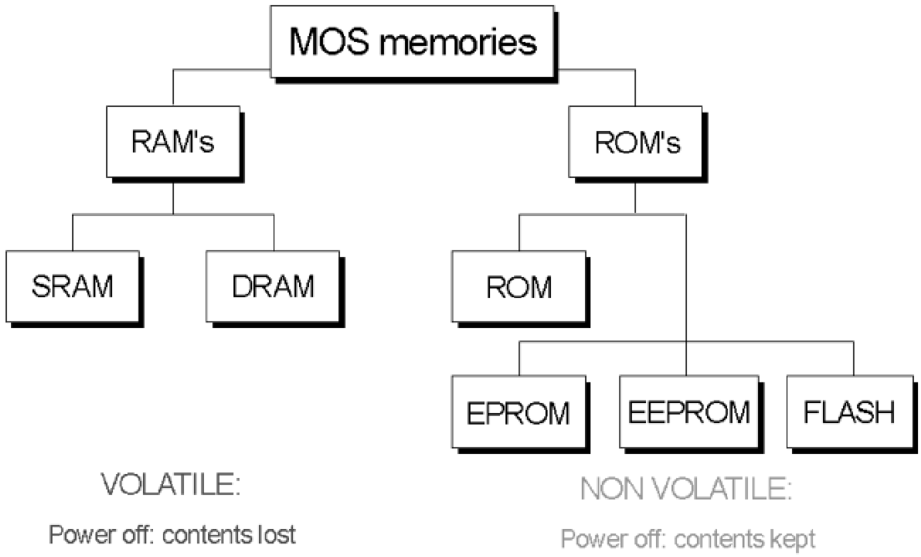


Figure 1. The categories of metal-oxide-semiconductor (MOS) memories.

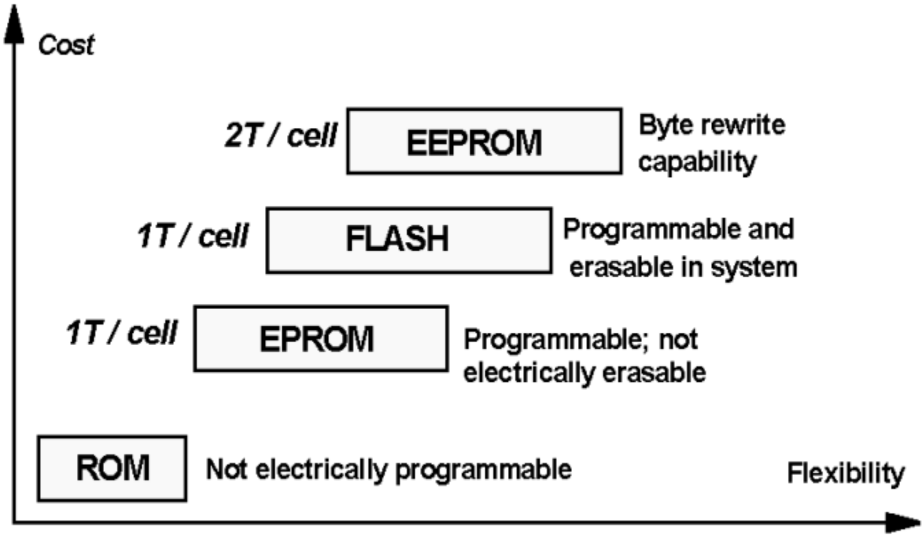


Figure 2. Non-volatile memory qualitative compared in terms of flexibility and cost.

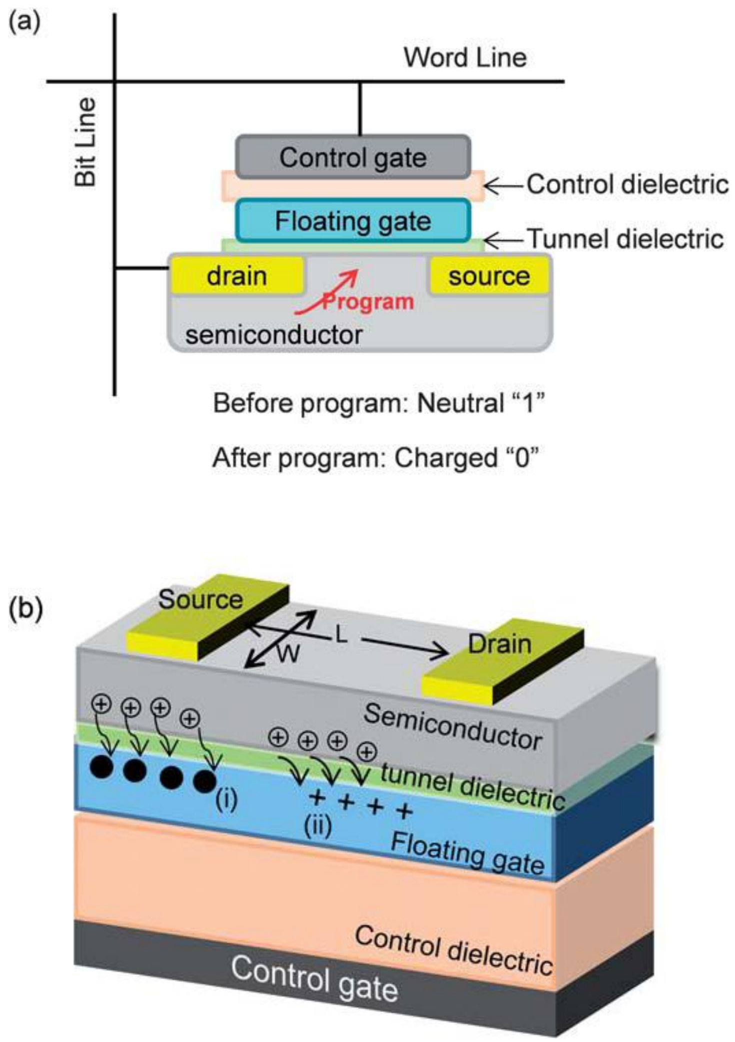


Figure 3. Schematic structure of (a) conventional flash memory, (b) charge trapping OFET-based memory device.

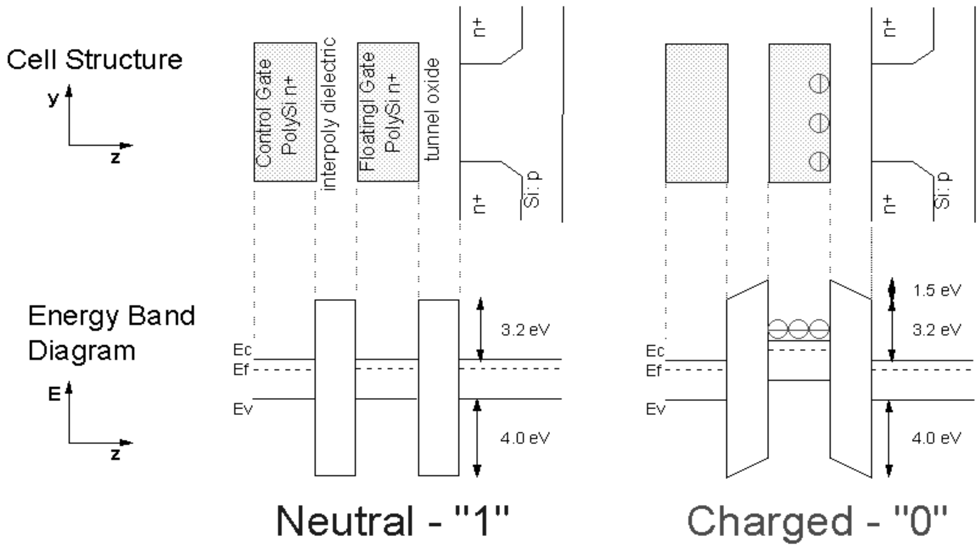


Figure 4. Schematic energy band diagram of flash memory with a semiconductor-insulator-metal-insulator-metal sandwich.

2. Experimental Procedures

2.1. Materials and Characterization

Myoglobin (from equine heart), hemoglobin (from human), cytochrome *c* (from equine heart), sodium phosphate monobasic, sodium phosphate dibasic, and pentacene were purchased from Sigma Aldrich and used without any further treatments. The heavily doped p-type Si wafer with a thermally grown 200 nm thick SiO_2 was used substrate. The memory properties of OFET memory devices were measured using an Agilent 4155B semiconductor parameter in the dark condition. All electrical measurements were conducted at room temperature and under air atmosphere without any device encapsulation.

2.2. Fabrication of the Charge Trapping Layer

A charge trapping layer, myoglobin, was prepared from sodium buffer solution at a pH of 7.2, in DI water. The myoglobin in 1 % buffer solution was stirred for overnight at room temperature. The myoglobin layer was fabricated by the spin-coating at 2000 rpm for 30 s. Prior to spin-coating, the substrate was exposed to ultra-violet ozone (UVO) for 30 min to uniformly coat the overall surface. Then the film was annealed at 80 ℃ for 1 hour in a hot plate.

2.3. Fabrication of OFET-based memory

The structure of OFET memory was fabricated in bottom gate, top-contact configuration (see Figure 5). A heavily doped p-type silicon substrate with a thermally grown SiO_2 layer (200 nm) acted as a gate electrode and a blocking insulator. Myoglobin thin layers were deposited onto the substrate via a spin-coating process with 0.05 mM to 1mM in 1 wt% buffer solution at intervals of 0.5mM concentrations. These films were annealed at 80 ℃ for 1 hour. For an organic p-type semiconductor in an OFET, a pentacene thin film was deposited by a thermal evaporation method under 3 x 10^{-6} Torr. The deposition rate of pentacene was 0.3-0.4 Å s^{-1} and thickness was 50 nm. Finally, to form the source and drain electrodes on the pentacene thin film, 100 nm thick gold electrodes were thermally evaporated through a shadow mask with a deposition rate of 4 Å s^{-1}. The evaporated source and drain electrodes had a channel length (L) and width (W) of 100 μm and 1,000 μm, respectively.

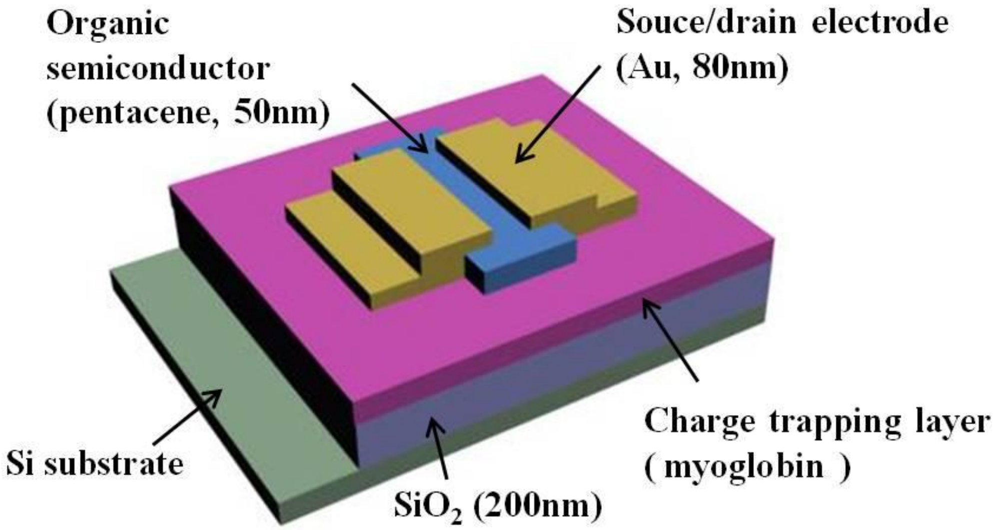


Figure 5. Schematic structure of the bottom-gate, top-contact OFET-based memory device including the myoglobin charge trapping layer.

3. Result and Discussion

3.1. Characteristics of Myoglobin Layer

The schematic configurations of a heme structure and myoglobin are shown in Figure 6 (a) and (b). The heme is composed of an iron atom contained in the center of large cyclic organic rings. The above mentioned myoglobin, which is a redox protein, consists of globin and one heme structure. To investigate the roughness and morphology of the spin-coated myoglobin layer, the topology and 3-dimensional atomic force microscopy (AFM) images of the myoglobin layer are shown in Figure 7 (a). The scanning electron microscopy (SEM) images of the layer are shown in Figure 7 (b). The value of RMS roughness and thickness of the fabricated myoglobin film was about 0.673 nm and 36 nm as measured, respectively. As a result, the obtained myoglobin layer was very smooth with uniform thickness ~ 36 nm.

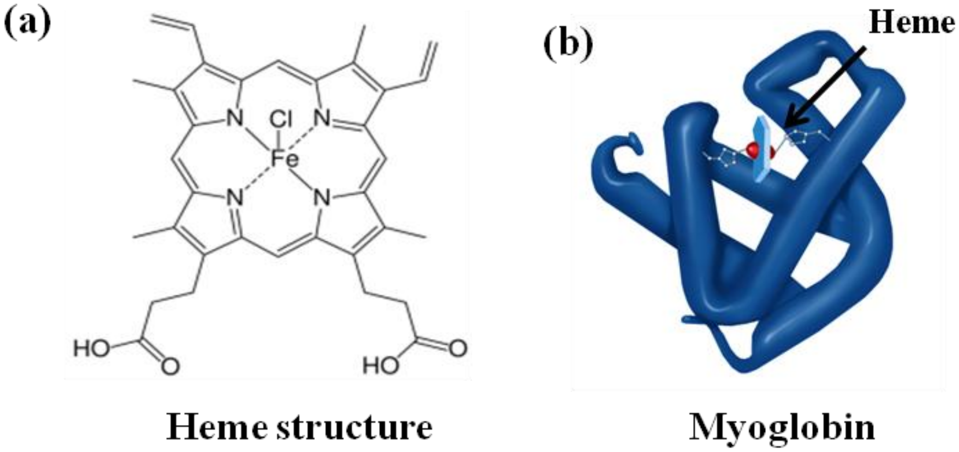


Figure 6. Structures of (a) heme and (b) myoglobin.

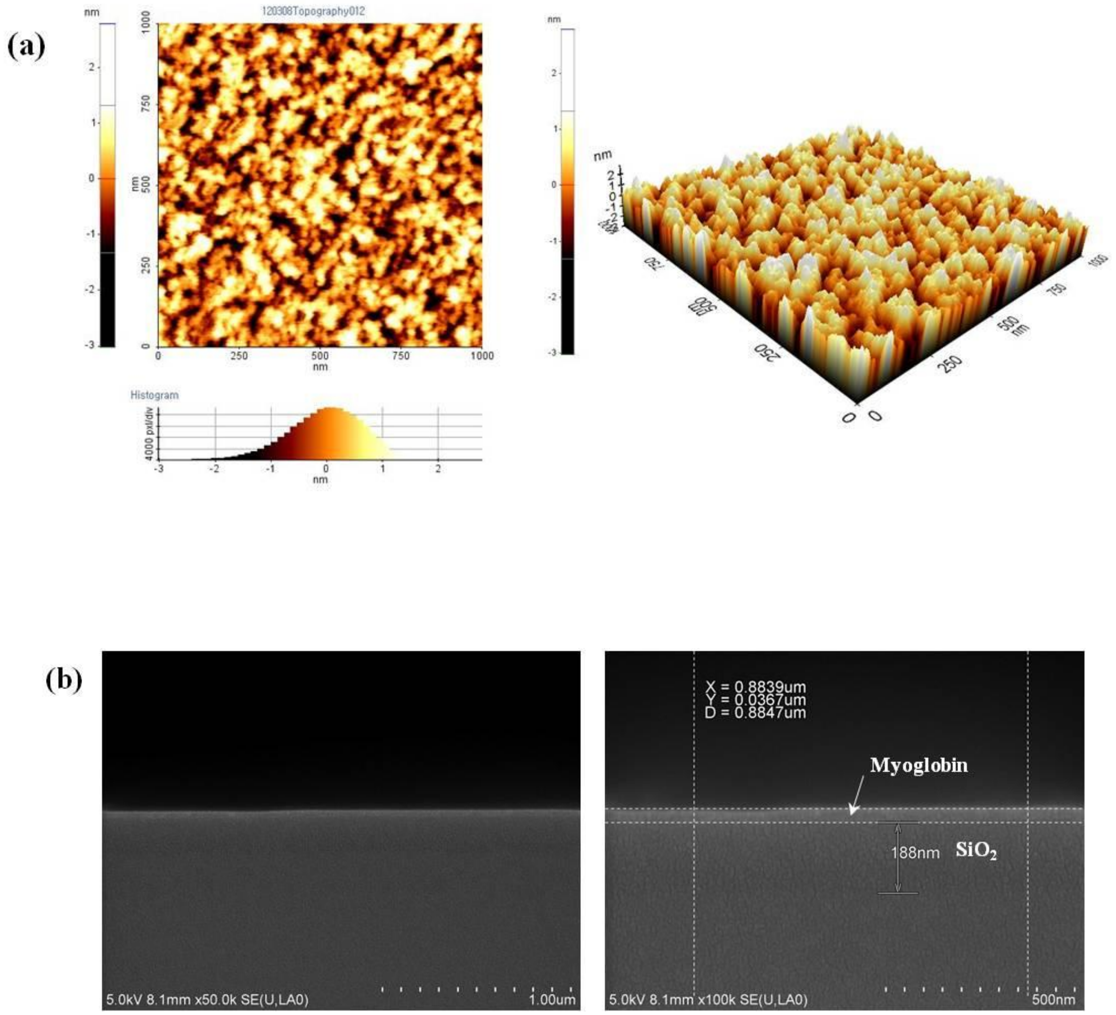


Figure 7. (a) AFM images and (b) cross-sectional SEM images of the myoglobin films prepared using 0.5 mM solutions. The myoglobin films were deposited by spin-coatingonto SiO_2 (200 nm) surface thermally grown on Si substrate

3.2. Transistor characteristics of OFET-based memory using Myoglobin as a Charge Trapping Element

We investigated the transistor properties of OFET-based memory including the myoglobin charge trapping layer with a bottom gate and top contact. First, transfer characteristics, which are one of the most important transistor properties, are exhibited in Figure 8. The myoglobin chargeable layer included OFET memory showed fairly good transfer characteristics compared with the myoglobin chargeable layer excluded OFET memory (the reference device) at a gate voltage sweep ranges 20 V to -40 V and the drain voltage of -40 V. The field-effect mobility (μ) was calculated from the following equation at the saturation region:

$$I_D = \frac{W\mu C_i}{2L}(V_G - V_T)^2$$

Where I_D is the drain current, μ the field-effect mobility of the semiconductor, V_T the threshold voltage, and C_i is capacitance per square centimeter of a dielectric layer. Used above the equation, the obtained field-effect mobility of the OFET-based memories including/excluding the myoglobin layer were 0.0574 $cm^2\ V^{-1}\ s^{-1}$ and 0.0721 $cm^2\ V^{-1}\ s^{-1}$, respectively. In order to obtain another importance factor of the transistor, output characteristics were measured at 8 V of a gate voltage step.

Figure 9 illustrates the output curve of the fabricated OFET–based memory including the chargeable layer using the myoglobin solution dissolved in buffer solution with 0.05 mM ratio (0.05mM myoglobin solution). As a result, the memory device demonstrated desirable organic transistor characteristics at a lower operating voltage than -40 V. Maximum saturation current of ~1.0 μA was achieved. The observed OFET characteristics were in good accordance with the conventional transistor models in both the linear and saturation behaviors at high drain voltages. The Table 1 shows mobility, threshold voltage shift, and an on/off ratio of the fabricated OFET consists of the myoglobin layer prepared using 0.5 mM solution.

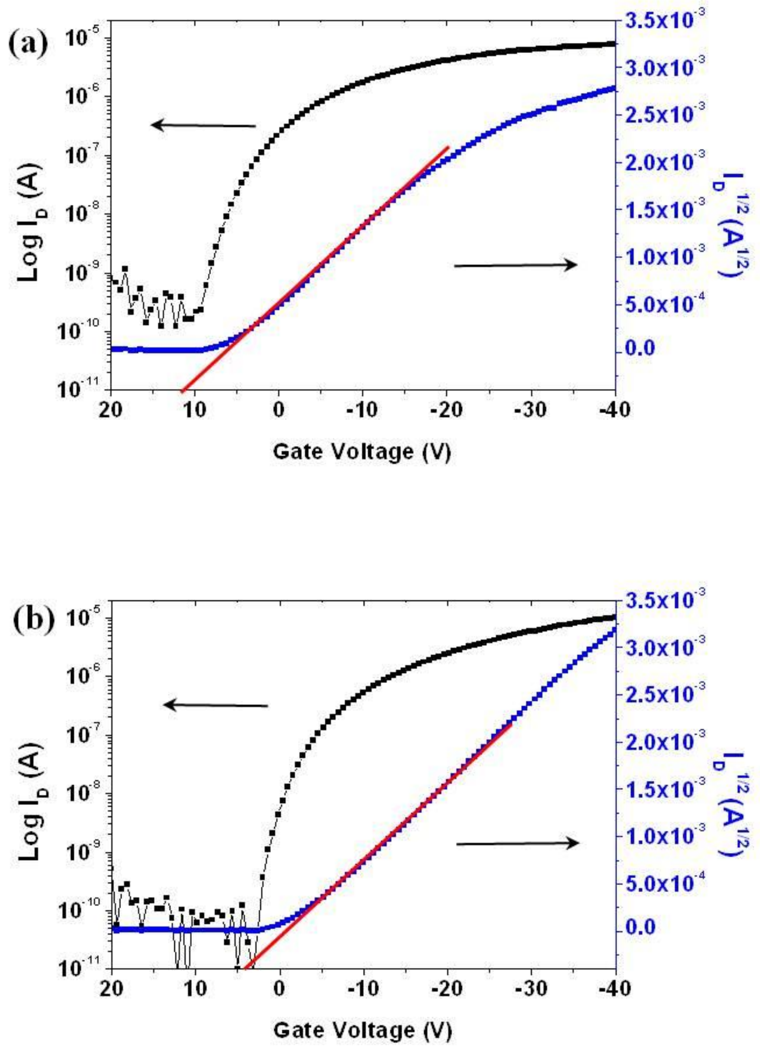


Figure 8. Transfer characteristics of OFET-based memory (a) including the myoglobin chargeable layer and (b) excluding the myoglobin chargeable layer at V_D = -40 V.

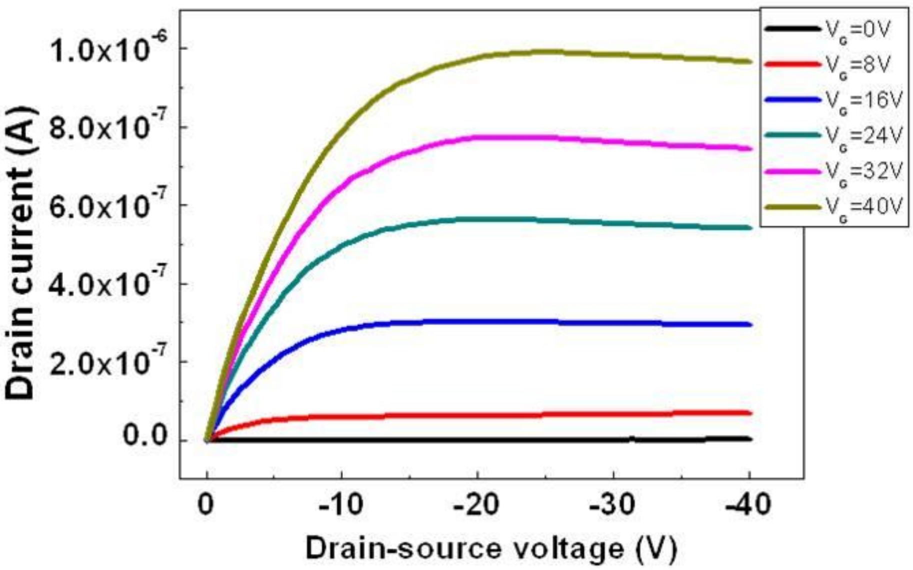


Figure 9. Output characteristics of OFET-based memory including the myoglobin chargeable layer prepared using 0.5 mM myoglobin solution. The gate voltage ranges from 0 V to -40 V in 8 V steps.

Redox protiens	Mobility ($cm^2V^{-1}s^{-1}$)	Threshold voltage shift (ΔV_T)	On/off ration	Thickness (nm)	Concentration (mM)
Myoglobin	0.0574	6.35	~10^5	36	0.5

Table 1. Electrical properties of OFET-based memory including myoglobin as a charge trapping element. (used 0.5 mM myoglobin solution.)

3.3. Performance of OFET-based Memory using Myoglobin as a Charge Trapping Element

In order to demonstrate the performance of OFET-based memory device composed of the myoglobin thin film as a charge trapping layer, we fabricated the OFET memory device and measured the memory properties. The transfer characteristics of the memory device according to the concentration of myoglobin solutions are presented in Figure 10. At a gate voltage sweep ranges 20 V to -40 V and the drain voltage of -40 V. The memory window was proportionally expanded with increasing concentrations of myoglobin solutions with the highest concentration, 1 mM. Maximum memory window of ~20 V was obtained in the fabricated OFET memory using the concentration of 1 mM myoglobin solution on application of programming and erasing operations. This result clearly presented that myoglobin successfully acted as a charge trapping site as expected. Figure 11 shows the transfer characteristics of OFET memory including myoglobin chargeable layer deposited by solution process using 1mM myoglobin solutions according to programming with -70 V for 2 s and erasing with -70 V for 2 s, respectively. The performances have changed with pH of sodium buffer solution (a) pH 5, (b) pH 7, and (c) pH 9. A clear memory window and the transfer properties were observed with pH 7, neutral state. In acidic and basic state, the heme structure and organic rings mainly constituted of the redox proteins were more prone to denaturation than the neutral pH.

Good endurance performance and data stability are essential for non-volatile memory applications to maintain stored information. The endurance properties of OFET memory devices with the myoglobin layer are showed in Figure 12. To measure the endurance characteristics of the transistor memory, the programming/erasing operations were repeatedly performed by the continuous application of bias pulse of ±70 V for 2 s. As shown Figure 12 (a), the variation of V_{th} was retained during 100 endurance cycles, one cycle that consists of one programming bias and one erasing bias. Figure 12 (b) shows a plot of (drain current) 1/2 versus gate voltage after applying the programming/erasing with 100 cycles.

A charge retention test was carried out and presented in Figure 13, which was acquired by the threshold-voltage shift as a function of the retention time under ambient conditions. The result of the fabricated OFET memory including myoglobin chargeable layer was obtained in the programming/erasing operations at an applied bias of ± 70 V for 2 s. In the initial V_{th} shift was 9.27 V that it slightly reduced to 6.36 V after 500 s, which amounts to about 30 % loss. As mentioned earlier, our fabricated memory devices did not contained the tunnelling dielectric layer since large organic rings in myoglobin may be acted as the tunneling insulator. Therefore, the stored charge carriers are prone to release from the charge trapping sites into the semiconducting channel because the prothetic groups are not dense layer. Also, Trapped charge loss corresponded to the degradation of the very thin-myoglobin layer because of the moisture in the air. This is the reason why OFET-based memory with myoglobin layer exhibited the relatively short retention time.

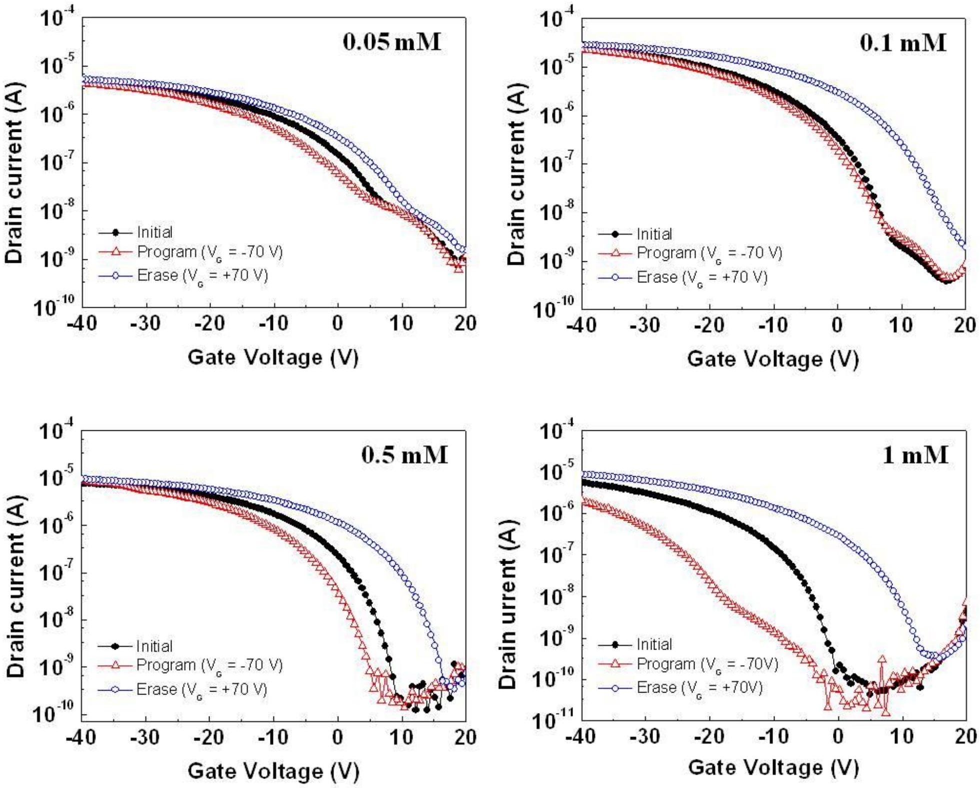


Figure 10. Transfer characteristics of OFET-based memory according to the concentration of myoglobin solutions after applying programming/erasing operation.

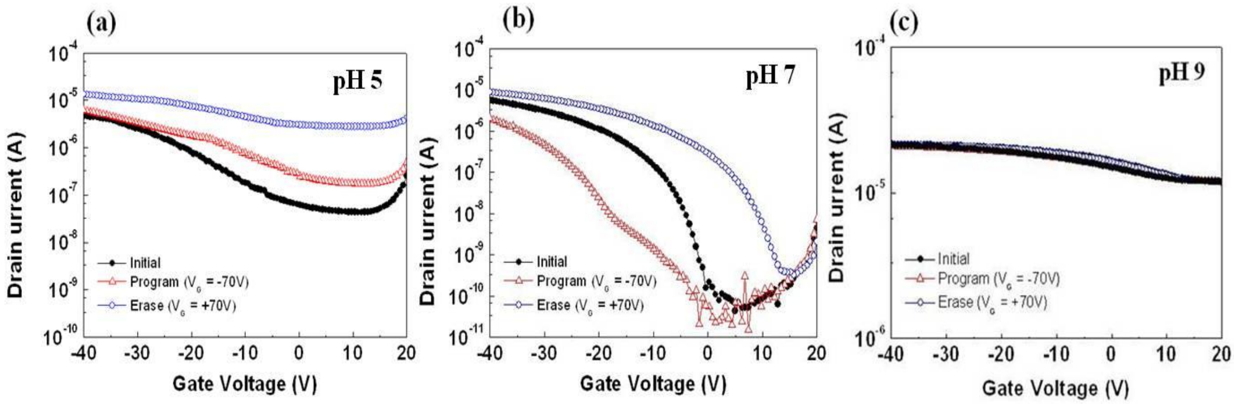


Figure 11. Transfer characteristics of OFET-based memory according to the pH of buffer solution using 1mM myoglobin solution after applying programming/erasing operations. The performances have changed with the pH of sodium buffer solution (a) pH 5, (b) pH 7, and (c) pH 9.

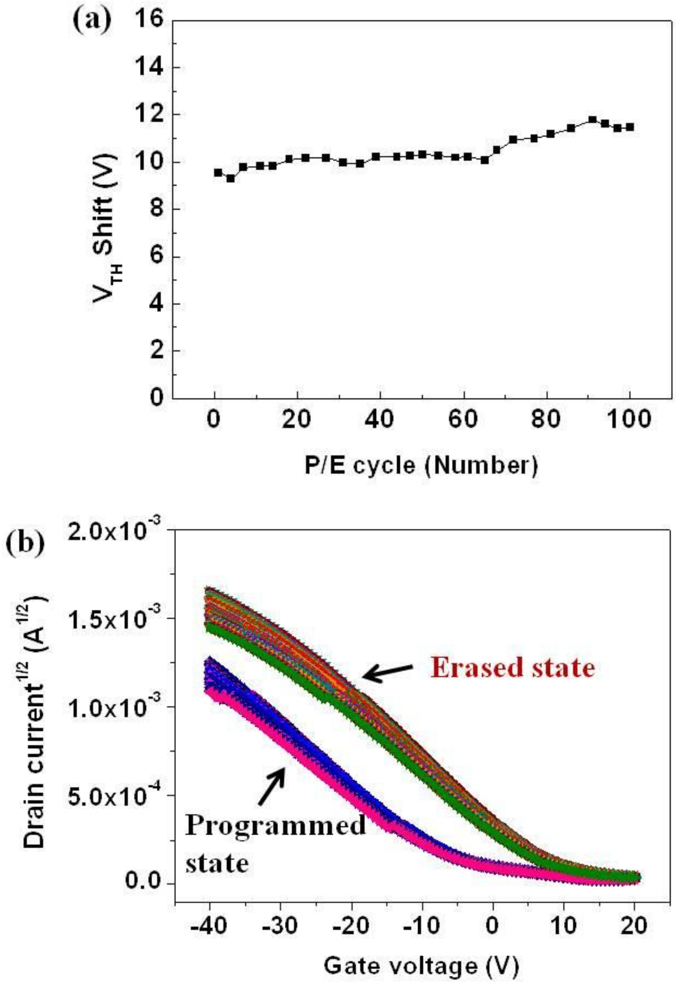


Figure 12. Performance of OFET-based memory including the myoglobin chargeable layer prepared using 0.5 mM myoglobin solution. The results were measured in ambient conditions at room temperature: (a) endurance test performed during 100 cycles and (b) transfer characteristics.

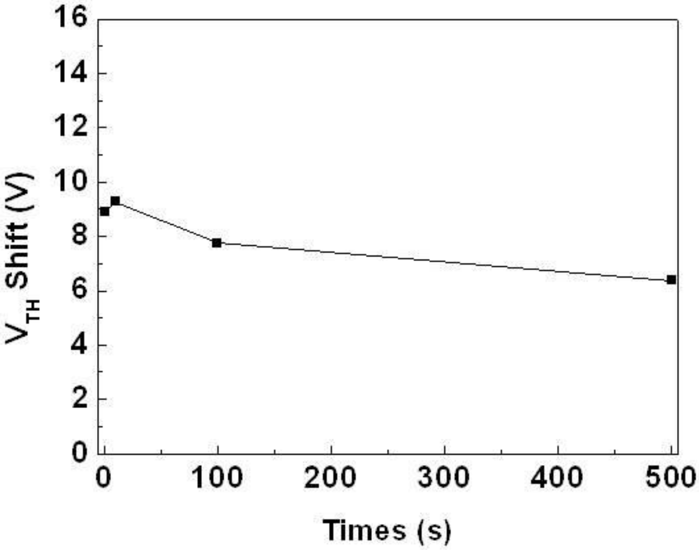
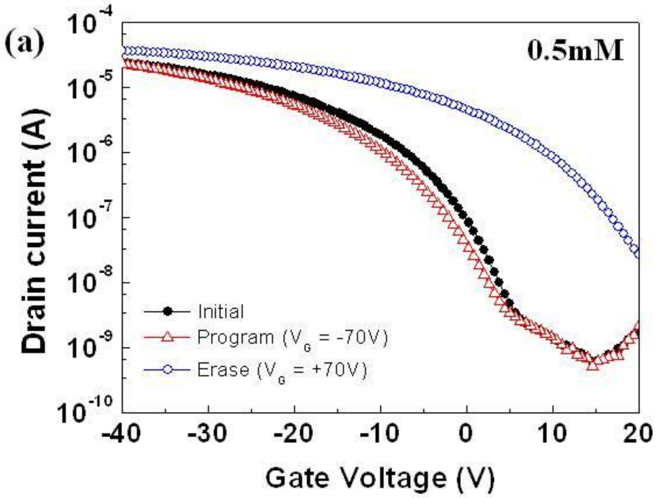


Figure 13. Retention characteristics as a function of the retention time for OFET-based memory including the myoglobin chargeable layer prepared using 0.5 mM myoglobin solution. The results were measured in ambient conditions at room temperature.

3.4. Performance of OFET-based Memory using Other Redox Proteins as a Charge Trapping Element

In order to examin the memory effect of redox proteins, we fabricated OFET-based memory device including other redox proteins as a charge trapping element. Figure 14 exhibits the transfer characteristics of OFET memory using (a) hemoglobin and (b) cytochrome c as a chargeable layer. Hemoglobin and cytochrome c are redox proteins and they also have the heme structure in the center. The obtained data demonstrate that the memory effect of redox proteins is due to the reversible redox reaction of the iron ion in the heme structrue. At a gate voltage swept from +20 to -40 V and drain voltage of -40 V, the V_{th} shifts of OFET-based memory using hemoglobin and cytochrome *c* as a charge trapping element were measured to be 20 V and 15 V, respectively. These V_{th} shifts were observed upon application of programming voltage (-70 V for 2 s) and erasing voltage (+70 V for 2 s) to the gate electrode. Therefore, we could confirm the charge trapping effect of redox proteins from the analysis of the obtained transfer characteristics.



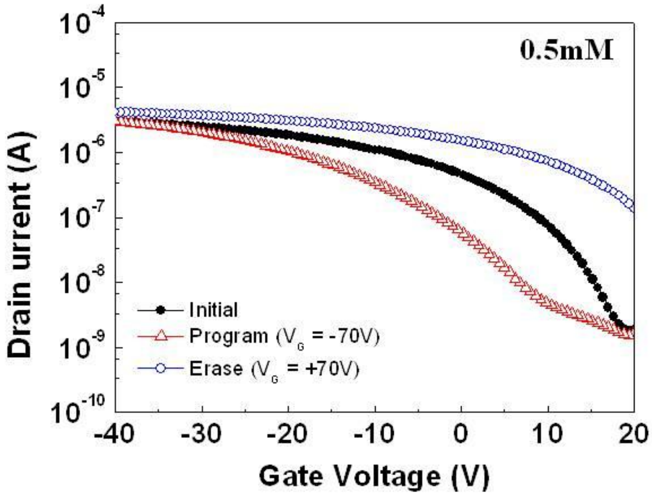


Figure 14. Transfer characteristics of OFET-based memory according to other types of redox proteins as a charge trapping element for determining considerable changes of threshold voltage after applying programming/erasing operations: (a) hemoglobin and (b) cytochrome *c*.

4. Conclusion

In this dissertation, we have presented for the fabrication of OFET – based memory device using myoglobin as well as other redox proteins as a charge trapping element. This non-volatile OFET memory device including the myoglobin chargeable layer showed a reliable large memory window and dependable endurance properties. The obtained memory window can be explaned via charge trapping effects of the heme structure in the redox proteins. The charge trapping layer was deposited by simple solution process using redox proteins solutions at low temperature.

In contrast with a conventional non-volatile memory devices, the fabricated OFET memory in this study did not require a tunneling dielectric layer, because the organic large rings in redox proteinscan be acted as the tunneling layer in the OFET memory devices

Although the memory performance need to be further improved and optimized, OFET memory based on redox proteins can be adopted to a variety of applications with potential to realize low cost, flexible, and large area data storage electronics.

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요약 (국문초록)

전자소자의 유연화, 대면적화가 필수조건으로 대두되면서 저렴하고 간단한 공정이 가능한 유기물을 이용한 소자들에 관한 연구가 꾸준히 진행되어 오고있다. 이런 추세에 따라서 다양한 전자소자를 이루고 있는 메모리 소자도 유연하고 간단한 프로세스로 제작하고자 하는 연구가 활발히 진행 중이다. 본 논문에서는 유기물 중에서도 우리 몸을 구성하고 있는 환원 단백질을 이용하여 비휘발성 메모리 소자를 제작하였다. 대표적인 환원 단백질로는 헤모글로빈, 미오글로빈 등이있다. 이러한 환원 단백질은 공통적으로 헴구조를 가지고있는데 헴구조는 전이금속이온 중에 하나인 철 이온을 가지고 있어서 가역적인 산화 환원 반응을 할 수 있다. 본 논문에서는 이러한 특성을 이용하여 환원 단백질 중하나인 미오글로빈을 비휘발성 메모리 소자에 적용하여 20 V 의 메모리 윈도우를 확인 하였다. 미오글로빈 이외에도 헤모글로빈, 사이토크롬씨와 같은 단백질이나 효소 또한 메모리 소자로 제작 했을 때 메모리 윈도우를 확인 할 수 있었다.

인체 내부에 있는 물질을 사용하여 전자소자를 제작하고, 신뢰할만한 성능을 얻을 수 있었다는데에 큰 의의가 있다.

가역적인 산화 환원 반응을 할 수 있는 환원 단백질은 메모리 뿐만 아니라 다른 유연한 전자소자에도 응용 될 수 있는 가능성을 가지고 있다.

Keywords: non-volatile memory, organic field-effect transistor memory, charge trapping, redox proteins, heme structure

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