Fabrication and characterization of non-volatile transistor memory based on polypeptide as gate dielectric

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Abstract. The organic thin film transistor (OTFT) fabricated with the polypeptide as a dielectric layer shows memory function. In order to investigate the effect of polypeptide structure on the performance of non-volatile transistor memory, the Fourier-transform IR (FT-IR) and Circular Dichroism (CD) spectral of PMLG film has been applied, respectively. In conclusion, the memory transistor device fabricated with polypeptide as the ferroelectric exhibit promising behavior such as a large memory window, and the dipole moment of the amide group was considered as the main source of the memory function.

1. Introduction

Recently, the non-volatile transistor memory array has been investigated extensively because it is an essential element for flexible electronic application such as in the memory card, radio frequency identification tag, e-signage and sensor[1-2]. As the first polyvinylidene fluoride PVDF and its derivatives based memory device was reported [3], there are lots of conjugated molecules and solution processable ferroelectric materials such as DNA [4,5,6], nylon [7], poly(imide) [8] are expected to realize the low-cost and low temperature fabrication process.

Poly (γ-methyl-L-glutamate) (PMLG), a synthetic polypeptide, can exist in various solid state, the preparation method and solvents which were chosen has great effect on the conformation forming [9,10]. A β-sheet structure is observed in films swollen in formic acid or in crystals precipitated from diluted solution in formic acid [11]. In most other solvents, the PMLG exist in the α helix conformation. Twisted structures similar to the cholesteric liquid-crystal state of the concentrated solution are retained in films prepared from dichloroethane solution[12, 13]. A gel which contains fibrous aggregations can be formed when the N, N-dimethylformamide (DMF) was applied as the solvent [14, 15]. The poorly-crystalline films were obtained from dimethylformamide (DMF) solution. In contrast, the films prepared from solutions in chloroform, dichloromethane (DCM) or m-cresol are highly crystalline, and consist of α helices arranged in a hexagonal lattice with dimension a=1.20 nm[16,17]. Therefore, understanding the film state is important to improve the performance of memory device from the viewpoint of their practical applications.

In this study, we demonstrated a top contacted ferroelectric polymer non-volatile transistor memory with PMLG and pentacene as a gate dielectric and semiconductor, respectively. The structure of the PMLG and the electronic performance including the transfer characteristic and output characteristic has been investigated. It is clearly seen that the fabricate device exhibit the memory behavior. And the relationship between molecular structure and memory mechanism has been presented successfully.
2. Experiment

2.1. Material
The PMLG (degree of polymerization: 440) were provided by Kyowa Hakko Co., Ltd. 1,2-Dichloroethane (Kanto Kagaku Co., Inc.) was used as received. Pentacene (Nard Institute Ltd. 98% purity) was used without further purification. Au (Sigma-Aldrich) was applied as source and drain electrode.

2.2. Preparation of the TFT device
PMLG film was prepared by spin-coating method onto the indium thin oxide (ITO) glass substrate with a 1,2-dichloroethane solution containing 3 wt. % PMLG. The thickness of the film was set to 800 nm. Pentacene film (thickness =50 nm) as an active layer was deposited on the PMLG film by vacuum deposition method under 2×10⁻³ Pa at a deposition rate of 0.2–0.4 Å/s. Au layer as the source and drain electrodes (W/L=5 mm/20 μm) was deposited by successive vacuum deposition on this pentacene layer. The structure of the OTFT memory and polypeptide are shown in Figure 1.

2.3. Apparatus
Circular dichroism (CD) spectra were recorded with the CD spectrometer (JASCO, J-820). Transmission Fourier-transform IR (FT-IR) spectra was measured at room temperature using FT-IT-660 Plus (JUSCO) equipped with an MCT detector. All electric measurements were carried out using a Keithley 4200 semiconductor parameter analyzer under dark conditions in vacuo.

Figure 1. The configuration of the OTFT memory device using PMLG as the gate dielectric.

3. Results and Discussion
In order to investigate the conformation of poly (γ-methyl-L-glutamate) (PMLG) film employed in this study, the CD analysis has been carried out. Figure 2 shows the CD spectra of PMLG in film state which was spin-coated on calcium fluoride substrate. As shown in the figure, either positive or negative CD signals have been obtained. For instance, the negative Cotton effect at about 205 nm and 230 nm have been observed. In addition, the positive Cotton effect about 196 nm and 210 nm have also been obtained. All of these signals indicated that the polypeptide used in this study is similar in shape to α helix structure, which is consistent well with the previously reported papers. [7-8] In addition, the shape of the spectrum was also consistent with that in the case of a clockwise interaction of the dipole moment of the PMLG main chain. [11] This implied that the formation of the helical structure is in a tertiary order, similar to a cholesteric liquid crystal phase.
Infrared spectroscopy (IR spectroscopy) which deals with the infrared region of the electromagnetic spectrum exhibits important information in the identification and investigation of the chemical materials. In this study, for the purpose of confirming the conformation of the PMLG film, IR spectroscopy has been carried out. In addition, through calculating the intensity ratio of amide 1 to amide 2, the orientation of the molecular axis of PMLG can also be determined by IR spectra. For instance, if the ratio of amide 1 to amide 2 is nearly the same, the molecular axis of PMLG will be oriented upright on the film surface. In contrast, when the PMLG molecules lie on substrates, namely, which is parallel with the film surface, the ratio will be remarkably higher.

Figure 2 shows the IR spectroscopy of PMLG film which is spin-coated on calcium fluoride substrate and analyzed by FT-IR absorption over a range of 1800–1500 cm⁻¹, and the left figure also illustrated the corresponding structure with the IR spectral. As the figure shows, the specific bands corresponding to the C=O ester has been well presented. In addition, the dipole groups with high dipole moment mainly including amide 1 and amide 2 groups also have been obtained, which is consistent well with its own structure. Further, based on the ratio of amide 1 to amide 2, it can be concluded that in the PMLG film, the molecules lie on the substrate.

Figure 3 shows the IR spectroscopy of PMLG film which is spin-coated on calcium fluoride substrate and analyzed by FT-IR absorption over a range of 1800–1500 cm⁻¹, and the left figure also illustrated the corresponding structure with the IR spectral. As the figure shows, the specific bands corresponding to the C=O ester has been well presented. In addition, the dipole groups with high dipole moment mainly including amide 1 and amide 2 groups also have been obtained, which is consistent well with its own structure. Further, based on the ratio of amide 1 to amide 2, it can be concluded that in the PMLG film, the molecules lie on the substrate.
Output characteristic is also one of the most important electronic characteristics of OTFT memory device, it can be obtained by measuring the $I_{DS}$ as a function of the voltage applied to the drain source electrode with a fixed gate voltage ($V_G$), as shown in Figure 4. It shows that the dependence of the drain source current $I_{DS}$ on the drain source voltage $V_{DS}$ for the devices using PMLG film as the dielectric layer, and it exhibits clear field effect with operation in p-type accumulation mode through applying negative gate bias. Compared with the DNA-CTMA based device, PMLG based device exhibits 10 times higher current densities. At the same time, only the linear region can be observed. Namely, the device gives a non-ideal $I_{DS}$ with less well-defined pinch off. It indicates that depletion layer in conducting channel was not formed at high $V_{DS}$ region, suggesting that the induced charge at the conducting channel may be originated from the spontaneous polarization of main chain dipole of PMLG molecule.

Figure 5 presents the transfer characteristic which represents the transistor current $I_{DS}$ plotted as a function of the gate voltage at constant $V_{DS}$ of the OTFT memory fabricated with PMLG as a gate dielectric layer. The observation of sizable hysteresis indicated that PMLG film can work as the
memory layer in the preparation of OTFT memories. The ON/OFF current ratio at $V_G=0 \text{ V}$ has been calculated as $2.79 \times 10^2$. At the same time, according to the plotting square root of $I_{DS}$ against $V_G$, the threshold voltage of -36 V was obtained. Further, the field effect mobility was calculated by fitting the plot of the square root of $I_{DS}$ versus $V_G$ using the following equation [18, 19, 20].

$$I_{DS}(\text{lin}) = \frac{W}{L} \mu C_i (V_G - V_{TH}) V_{DS}$$  \hspace{1cm} (1)

Where $I_{DS}$ is the drain source current; $C$ is the capacitance of gate dielectric per unit area; $V_G$ is the gate voltage; $V_{TH}$ is the threshold voltage, $W$ and $L$ are the width and length of the channel of the device, respectively. The capacitance was measured to be 0.424 nF/cm². The carrier mobility of the PMLG based device was calculated to be $1.09 \text{ cm}^2/\text{V}\cdot\text{s}$. To our best knowledge, it is the moderate mobility reported for a bottom gate top contact organic semiconductor TFT memory device based on PMLG gate dielectric.

4. Conclusion

In conclusion, we demonstrated a non-volatile transistor memory device based on PMLG as the ferroelectric dielectric layer. A high mobility up to $1.09 \text{ cm}^2/\text{V}\cdot\text{s}$ was obtained. Based on the study of the Circular Dichroism and Infrared spectroscopy, it indicated that the PMLG applied in this experiment possess the helix structure, and the PMLG molecules lie on the substrate. Combined with the electronic performance of the memory device, it reveals that the dipole moment in the main chain is the main source of the memory property.

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