Fabrication of Ferroelectrics-Gate Field Effect Transistors with Layered Structure of Small- Molecular Ferroelectrics / Organic Semiconductors

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Abstract

For the development of lightweight and flexible organic electronics, many organic molecular materials have been developed. In particular, hydrogen-bonded organic ferroelectrics are expected to realize ferroelectrics-gate FETs (FeFETs), which are used as nonvolatile memory, with low-voltage drive due to their small coercive electric field. However, FeFETs have not been fabricated with hydrogen-bonded organic ferroelectrics because of their low tolerance for solvents and heat, which makes it difficult to stack other functional layers on them. In this study, we used a recently developed thin-film transfer method to laminate organic semiconductor (OSC) and metal electrodes onto hydrogen-bonded organic ferroelectrics. FeFETs were successfully fabricated, and their low-voltage operation was demonstrated.

Authors

Yohei Uemura is engaging in the research of the material science in organic ferroelectrics. In this study, Y. Uemura is responsible for the fabrication of the thin films of organic ferroelectrics and polymeric semiconductors, and a part of the electrical characterization.

Tatsuyuki Makita is engaging in the research of the electronics devices based on the single-crystal thin films of OSC. In this study, T. Makita is responsible for the fabrication of the layered device structure by transferring the OSC films and metal electrodes, and a part of the electrical characterization.

1. Background

Electronic devices using organic molecules are attracting attention as the next-generation electronics industry because they are lightweight, flexible, and can be easily manufactured by printing. So far, various high-performance organic electronic materials have been developed through the designing of molecular structure. However, organic materials tend to be damaged by solvents or heat due to their weak intermolecular interaction, which makes it difficult to fabricate electronic devices with the sequential deposition of functional

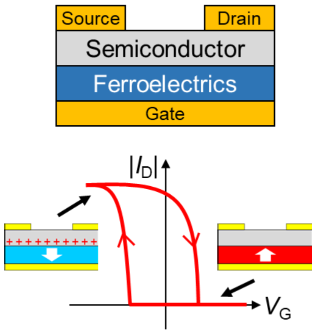

Figure 1.1 Schematics of the structure and I_D–V_G characteristics of FeFET.

layers. Therefore, it is essential to develop both materials and device fabrication processes for the development of organic electronics.

One of the important devices in electronics is the ferroelectrics gate transistor (FeFET), which operates as a non-volatile memory. Ferroelectrics are a class of insulator, which have the reversible spontaneous polarization used in FeFETs, sensors and actuators. As shown in Fig. 1.1, FeFETs consist of a gate electrode, ferroelectrics, semiconductor, a source electrode and a drain electrode. If p-type semiconductor is used, the current from source to drain electrodes (I_{D}) is turned on when the spontaneous polarization of ferroelectrics is downward due to the carrier induction, while I_{D} is turned off when the polarization is upward. The direction of spontaneous polarization can be controlled by the voltage between source and gate (V_{G}). Since the spontaneous polarization is maintained even if the V_{G} is zero, the on or off state of I_{D} can be preserved without continuous power supply.

Since the on/off ratio and the driving voltage of FeFET depend on the spontaneous polarization and coercive electric field of ferroelectric materials, it is essential to develop the ferroelectric materials. So far, many ferroelectric materials composed of organic molecules have been reported [1]. In particular, 2-methylbenzimidazole (MBI), a type of hydrogen-bonded type organic ferroelectrics, has a small coercive electric field (11 kV/cm at 0.2 Hz) and a large spontaneous polarization (5.2 kV/cm), suggesting that it is a suitable material for the low-voltage driven devices [2, 3]. However, MBI has not been used for FeFETs because of its low tolerance for solvents, which makes it difficult to laminate it with other materials.

Regarding this issue, T. Makita *et al*. have recently reported techniques for transferring OSC thin films and patterned metallic electrodes [4, 5]. A schematic illustration of a procedure to transfer OSC single crystals is shown in Figure 1.2(a). An OSC film fabricated on a template substrate which has superhydrophilic surface is placed on the destination substrate. Then, a few droplets of water were applied near the point of contact between the two substrates. The difference in the surface energy of the template substrate and the OSC film, which has the highly hydrophobic surface, leads to the water infiltration between the OSC and the template substrate. This technique allows formation of OSC films on the underlayers which cannot be used normally. A schematic illustration of a procedure to transfer metallic electrodes is shown in Figure 1.2(b). After patterning electrodes on the substrate with a release layer, polymer thin film with a thickness of 100 nm is formed. Then, a water-soluble polymer layer with a thickness of 20 to 30 µm is fabricated to be easily handled. By

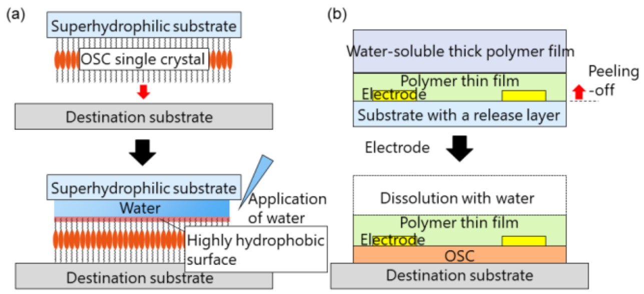

Figure 1.2 Schematics of the transfer method. (a) The transfer of films of OSC single crystal. (b) The transfer of metal electrodes.

peeling off the resulting film from the substrate, an electrode embedded film can be obtained. Finally, the film is placed on the destination substrate with moderate heating followed by application of a few droplets of water to dissolve water soluble polymer layer, which results in adhesion of electrodes with electrostatic force of thin polymer layer. With this method, electronic devices can be fabricated without giving any damage on the destination substrate during the formation of patterned electrodes. These two techniques have raised the possibility to integrate the materials which have been difficult to be employed in layered structures.

2. Purpose of research

In this study, we aim to realize a FeFET using MBI as a ferroelectrics layer. For this purpose, we establish a method to transfer OSCs and metal electrodes onto MBI thin films without damaging the MBI films. We characterize the polarization reversal and the FeFET operation in the fabricated layered structure.

3. Experiment

3.1. Fabrication of bottom-gate structure

The single-crystal MBI films (Figure 3.1 (a)) were fabricated on a doped Si substrate by confining the N,N-dimethylformamide solution (0.75 wt%) in the narrow space between the Si substrate and a glass plate coated with hydrophobic fluorinated polymer. After the slow evaporation of the solvent and the crystal growth, the glass plate with the fluorinated polymer layer was detached from the Si substrate with MBI films. A single-crystal OSC film fabricated on another substrate was transferred and stacked on MBI films as described below.

A single crystalline film of C9-DNBDT-NW (Figure 3.1 (b)), which is one of DNBDT analogs [6], was fabricated on a glass substrate treated with UV/O_3 via continuous edge-casting technique [7]. This technique, schematically described in Figure 3.1 (c), is one of the printing techniques which can give large-area single crystalline films by moving the substrate with continuous supply of the semiconductor solution. Then, the resulting single crystalline thin film was laminated on the MBI single crystal by using the transfer method for semiconducting film [4].

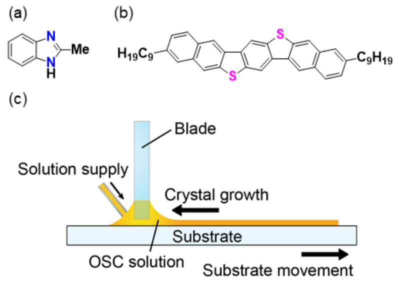

Figure 3.1 Schematics of materials and film fabrication. Chemical structure of (a) MBI and (b) C9-DNBDT-NW. (c) Schematics of the continuous edge-casting method.

Thickness of the MBI film：550nm、thickness of the C9-DNBDT-NW film：12nm。

3.2. Fabrication of top-gate structure

The source and drain electrodes were fabricated on a glass substrate by vacuum deposition, on which the thin film of P3HT [8], a polymer OSC, was deposited by spin coating the chlorobenzene solution (0.4 wt%) at 2,000 RPM. Polycrystalline films of MBI were fabricated on the P3HT film by spin coating the ethanol solution (15 wt%) at 1,000 RPM after trimming the P3HT film around the source and drain electrodes with a micromanipulator. The P3HT film was trimmed to form grooves to hold the solution of MBI, which is hard to spread on the P3HT surface. The gate electrodes were fabricated on another substrate and transferred on MBI films as described below.

A self-assembled monolayer of decyltrimethoxysilane (DTS) was formed on the surface of glass substrate by vapor deposition (Figure 3.2(a)). After the deposition of gold layer by vacuum evaporation, photolithography process was performed to form the pattern of gate electrodes using a positive photoresist, AZ 5214E (MicroChemicals). Subsequently, poly(methyl methacrylate) (PMMA) was spin-coated (2000 RPM) on top of the electrodes to a thickness of 100 nm using 5 wt% butyl acetate solution followed by annealing at 80 °C for 30 min. Then, an aqueous solution of 5 wt% poly(vinyl alcohol) (PVA) was applied on top of PMMA as a 20– to 30–μm-thick handling layer. After dried at 50 °C for 2 h, the resulting film was peeled off from the DTS treated glass substrate. The obtained film was placed on the surface of polycrystalline thin films of MBI at 60 °C followed by application of water to dissolve the PVA layer (Figure 3.2(b)). Finally, the residual PVA was completely removed by stirred in water at 30 °C for 2 h.

Thickness of source and drain electrodes：32 nm (Cr: 2 nm, Au: 30 nm)、 Thickness of the P3HT film：14 nm、 thickness of the MBI film：1,500 nm、thickness of gate electrodes：40 nm.

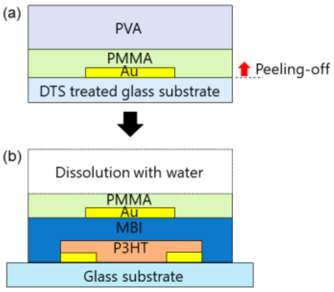

Figure 3.2 Schematics of the transfer method of gate electrode for the fabrication of top-gate structure. (a) Fabrication of electrode embedded films. (b) Lamination of electrodes on the surface of MBI.

4. Results and discussions

4. 1. Bottom-gate structure

We first fabricated the bottom-gate structure of MBI and C9-DNBDT-NW (Fig. 4.1 (a)). The single-crystal nature of the MBI films fabricated on a Si substrate (Fig. 4.1 (b)) was confirmed by crossed Nicols micrographs (Fig. 4.1 (c)). Microscopic and crossed Nicols micrographs of MBI film did not show apparent changes after the lamination process (Fig. 4.1 (d, e)), confirming that MBI was not damaged. We have succeeded in stacking the OSC single-crystal films on the MBI film for the first time using the transferring process that solvents do not contact with the base layer.

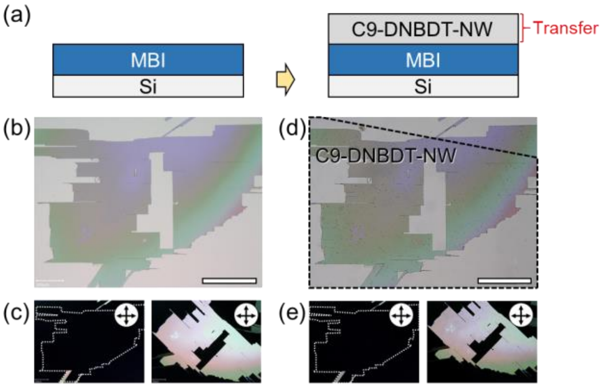

Figure 4.1 The fabrication of bottom-gate structure. (a) Schematics of the fabrication process of bottom-gate structure. (b, c) (b) Microscope image and (c) crossed Nicols micrograph of an MBI single-crystal film fabricated on Si substrate. (d, e) (d) Microscope image and (c) crossed Nicols micrograph after C9-DNBDT-NW is transferred. Black dashed frame indicate the C9-DNBDT-NW film。 Scale bar: 400 μm.

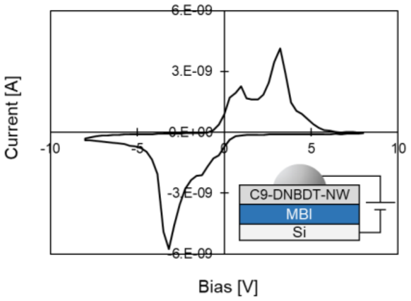

Figure 4.2 Measurement of the polarization reversal of MBI / C9-DNBDT-NWlayered structure.

A droplet of liquid metal eutectic Ga–In (EGaIn) was placed in contact with C9-DNBDT-NW and bias was applied between Si and EGaIn to measure polarization reversal of MBI (Fig. 4.2). The peaks of displacement current due to the polarization reversal of MBI is clearly observed at around ±3 V, indicating that the low-voltage driving of devices is possible even after the semiconductor is transferred on MBI.

Though we tried to measure the FeFET characteristics using two EGaIn droplets as the source and gate electrodes, drain current I_D was not observed. The injection of carrier from EGaIn into C9-DNBDT-NW may be prevented by the large difference between the work function of EGaIn (4.2 eV) and the HOMO level of C9-DNBDT-NW (5.2 eV) [6]. In addition, the roughness of MBI surface may inhibit the carrier conduction at the MBI/C9-DNBDT-NW interface. The result of atomic force microscopy (AFM) indicates that the MBI surface have the roughness of a few nm (Fig. 4.3).

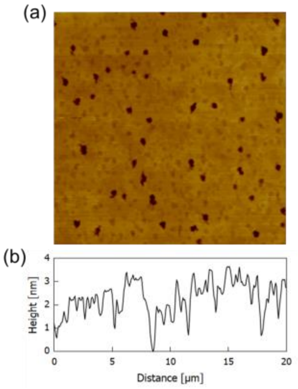

Figure 4.3 Surface roughness of an MBI single-crystal film. (a) AFM image measured on an MBI film. (b) A line profile of (a).

4. 2. Top-gate structure

From the investigation of the bottom-gate structure, we consider that it is difficult to use the MBI surface as the channel, so we next fabricated the top-gate structure (Fig. 4.4 (a)). It is expected that the better electrical conduction than that of the bottom-gate type can be obtained by the use of smooth surface of polymeric semiconductor as the channel. The layered structure of P3HT / MBI was successfully fabricated by simple spin coating method (Fig. 4.4 (b, c)). Furthermore, it is found that gate electrodes can be stacked on the MBI film without damaging MBI using the transfer method (Fig. 4.4 (d)).

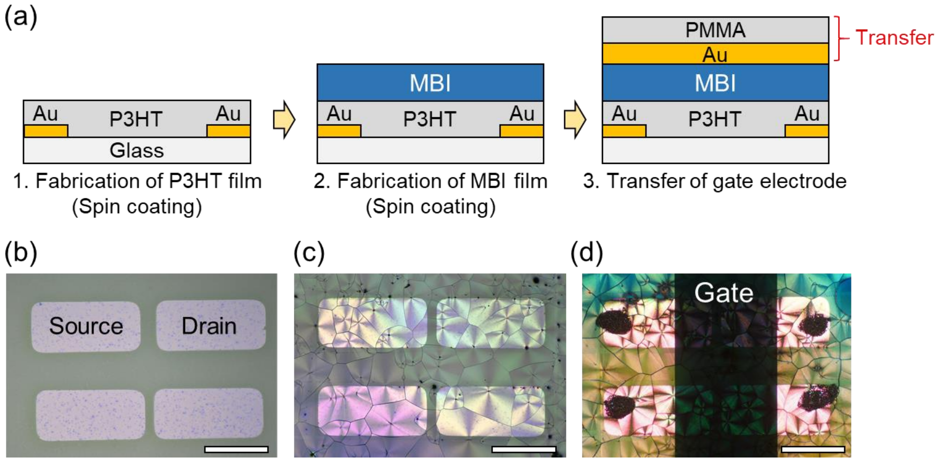

Figure 4.4 The fabrication of top-gate structure. (a) Schematics of the fabrication process of top-gate structure. (b - d) Microscope image at each step shown in (a). (b) A film P3HT fabricated on the glass substrate with source and drain electrodes. (c) The MBI polycrystalline film fabricated on the P3HT film. (d) The gate electrodes transferred on the MBI film. Scale bar: 400 µm.

The I_D - V_G characteristics of the fabricated top-gate FET shows the hysteresis due to the polarization reversal of MBI, indicating that the device operates as the FeFET memory (Figure 4.5 (a)). The peaks in I_G - V_G characteristics also indicates that the spontaneous polarization of MBI was reversed (Fig. 4.5 (b)). The low-voltage operation of ±15 V was achieved using the relative thick MBI film of 1.5 µm due to the small coercive electric field of MBI, indicating that MBI is an advantageous material for the development of low-voltage driven FeFETs.

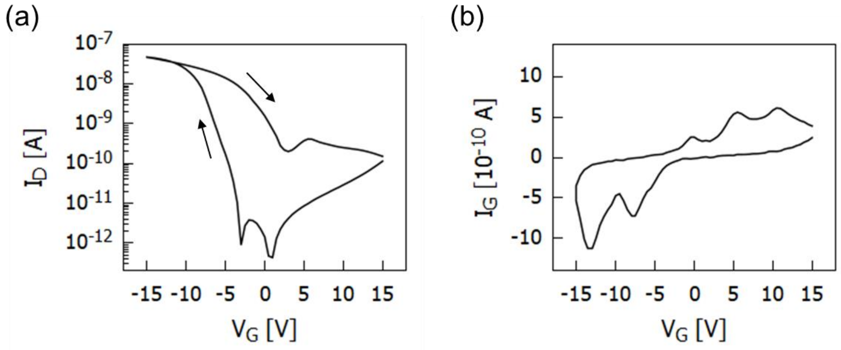

Figure 4.5 FeFET characteristics of a fabricated FeFET. (a) I_D-V_G characteristics and (b) I_G-V_G characteristics of a top-gate FeFET. V_D = -5 V, L = 50 µm, W = 340 µm.

5. Conclusion

By using a new transfer method, we have succeeded in stacking OSC thin films and metal electrodes on hydrogen-bonded organic ferroelectrics of MBI, which is easily damaged by solvents and heat. We fabricated the FeFET using MBI as insulating layers, and observed low-voltage memory operation for the first time. In the future, it is necessary to evaluate the characteristics that are essential for practical application, such as the retention time of the polarized state and fatigue resistance to the polarization reversal. In addition, it is expected to be possible to realize devices that operate at lower voltages by fabricating thinner MBI layers.

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