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Solution-processed conformal coating of ferroelectric polymer film and its application to multi-bit memory device

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ABSTRACT

Ferroelectric multi-bit storage memory which is fabricated by means of the patterning and double-coating of ferroelectric polymer film is demonstrated. The multi-bit memory device demonstrated here has two thicknesses in a capacitor. Therefore, ferroelectric switching at each thickness arises in different voltage range. The structured capacitor with two different thicknesses is realized by optimizing two processes, i.e., the photo-lithographical patterning of the ferroelectric film and a double-coating method for the formation of the multilayer structure. Not only photo-lithographical patterning but also the double-coating method of ferroelectric film was performed with a solubility-controlled ferroelectric polymer solution created by the addition of an insoluble solvent. From electrostatic force microscopy and displacement-voltage measurements, the fabricated multi-bit storage memory operated as predicted for a multi-bit memory scheme. The solubility-controlling method suggested here will offer additional promising routes to fabricate complex organic devices based on a solution process.

1. Introduction

Recently, ferroelectric polymers based on vinylidene fluoride (VDF) have been attracting research attention owing to the simplicity of related processes and to their remarkable material features. In terms of the processes, ferroelectric film can be formed by various means, such as physical vapor deposition [1], chemical vapor deposition [2], the Langmuir-Blodgett method [3,4] or by solution processes [5–8]. By changing the molecular structures chemically with different moieties, their physical properties could also be modulated [9,10]. Mechanical flexibility and optical transparency in the visible range make ferroelectric polymers feasible for use in transparent conducting film applications [11]. Their additional environmental inertness offers the possibility of a nonvolatile memory medium [12].

Utilizing these properties of ferroelectric polymers, applications as multi-bit memory media have been reported. In one study [13], it was demonstrated that the morphology of ferroelectric polymer film was manipulated by simple indentation with a rigid molding, resulted from a capacitor consisting of two different thicknesses. This type of capacitor can operate as a multi-bit memory device if a top electrode covers the two areas with different thicknesses at the same time. This structure is described in Fig. 1. For a clear understanding of its operation, we assume that the region with a thin thickness and the relatively thick region are designated as capacitor A (C_A) and capacitor B (C_B), respectively. When the remanent polarization in ferroelectric film is initially upward (i.e., a negative external voltage applied at the top electrode while bottom electrode is connected to the ground.), we define the logic state as 11. When external voltage (V_A) is applied between the coercive voltage of C_A (V_{CA}) and the coercive voltage of C_B (V_{CB}), only the dipoles in C_A are switched, resulting in logic state 10. Applying a V_A value smaller than V_{CB} cannot switch the dipoles in C_B. When continuing to increase the value until it exceeds V_{CB}, V_A can switch the dipoles in C_B, resulting in the 00 state. From the 00 state, a $|-V_A|$ value between $|-V_{CA}|$ and $|-V_{CB}|$ makes the dipoles in C_A reverse again, resulting in the 01 state. Likewise, when $|-V_A|$ is larger than $|-V_{CB}|$, the overall polarization state returns to the initial state, 11. Therefore, four logic states are addressable by tuning the amplitude and polarity of V_A. The proposed scheme shows that the maximum operating voltage (V_{MAX}) depends on the thickness of C_B. Moreover, the thickness of C_A must be scaled down for the distinct separation of all of the states. However, an indentation process is inappropriate when seeking to realize a thin film below 100 nm, though the fabrication of such a film can be achieved by means of one-step pressing. As a result, the thickness of C_B needs to be thick enough for indentation. Compared to inorganic ferroelectric film such as lead zirconium titanate (PZT), the coercive field (E_C) of the ferroelectric polymer film is 10 times higher than the E_C of PZT. Therefore, there is no choice for a low-voltage operating ferroelectric system but to reduce the film thickness. An additional practical problem is expected in that the rigid molding for indentation may perish due to repetitive pressing.

Another study [14] also demonstrated that the morphology of ferroelectric polymer film was manipulated by hybridized process of photolithographical patterning and transferring of ferroelectric polymer

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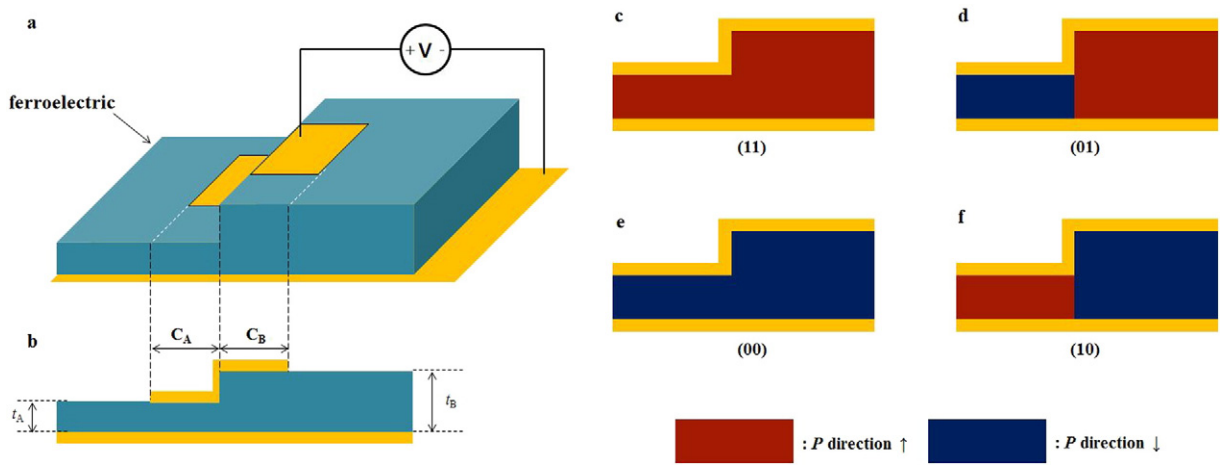

Fig. 1. Schematic of the ferroelectric multi-bit memory: (a) 3-D device structure of the multi-bit memory; (b) 2-D device structure of the multi-bit memory, where C_A and C_B refers to each capacitor with thicknesses of t_A and t_B, respectively. (c) Initial logic state, 11 (d) logic state, 01 (e) logic state, 00 (f) logic state, 10.

film. Compared with the indented case, the maximum operating voltage was reduced below 20 V. This reduction of the maximum operating voltage could be achieved by reducing the film thickness, which was fabricated by transferring of a spin-coated thin polymer film. Though the transferred film was also fabricated by spin-coating process and it could have superior dielectric properties before it is transferred, film uniformity is expected to be wrinkled, folded and torn after the transfer process is done as the transferred film is large. Such nonuniformity caused by microscale damage may confine the applicability of transfer-based process to small and rigid wafer-scale fabrication. Therefore, a breakthrough to minimize such nonuniformity in thin and large-area film is strongly required.

Thus, approach to direct spin-coating process on a patterned ferroelectric film need to be considered as an alternative to transfer process. As is well-known, it is through the spin-coating method that the thickness of a polymer film is precisely and uniformly controlled. To control the film thickness, there are many variables, such as the spin speed, spin time, solute concentration, and solvent properties, which must be considered. So, spin-coating is considered to be a highly suitable method for the fabrication of ferroelectric devices which operate at low voltages in large and flexible substrate. Moreover, conformal coating of ferroelectric polymer film can be achieved if solvent is well selected. In this work, it is demonstrated that multi-bit memory can be fabricated by the patterning and double-coating of ferroelectric polymer film such that the multi-bit memory can also operate below 20 V. The essential technology involves a double-coating method to create a multi-layer structure. To hinder the dissolution of the pre-deposited ferroelectric film, the solubility of the solution to deposit upper film was controlled by the blending in of an insoluble solvent.

2. Experiment

2.1. Ferroelectric film formation

For the ferroelectric polymer solution, poly(vinylidene fluoride-*co*-trifluoroethylene) (P(VDF-TrFE), 75/25 mol%, Elf Atochem, CAS No.: 28960-88-5) was purchased and dissolved in a solvent, methyl-ethyl-ketone (MEK) at various concentrations. The solvent MEK was selected as main solvent because the vapor pressure (VP) of MEK is quite high (78 mm Hg) so the almost solvent can vaporize for spin-coating process, which enables ferroelectric film to be coated uniformly on the surface of substrate. For the case of a solvent with a low VP such as cyclohexanone (5 mmHg), in contrast, ferroelectric polymer solution can flow after spin-coating process and can change the final morphology of device. After complete dissolution with stirring, a polytetrafluoroethylene filter with a pore size of 0.22 μm was used to remove dust particles. The nonlinear variables of the spin speed and the spin time of the spin-coating process were fixed at 1500 rpm and 10 s, respectively. As a result, the thickness of the ferroelectric film could be controlled almost linearly according to the ferroelectric polymer concentration of the solution. At 1 wt% (we define wt% as (mass (gram) of solute per volume of solvent [unit: g/mL]) × 100), the thickness of the ferroelectric film was approximately 90 nm. After spin-coating, the sample was annealed at 130 °C on a hot plate for 1 h to remove any solvent residue and increase the crystalline β-phase. The thickness of the ferroelectric film was measured using an α-step profilometer (Dektak 6 M, Veeco Instruments, Inc.).

2.2. Patterning of ferroelectric film

The ferroelectric polymer film (FPF) was patterned using conventional photo-lithography technology, which enables the edges of the patterned ferroelectric polymer film to be defined clearly. For the first procedure, FPF of 90 nm was spin-coated onto an Au-deposited SiO_2/Si wafer. A commercially-available g-line (436 nm)-sensitive photoresist (AZ 1512, AZ electronic materials) was deposited and soft-baked at 95 °C for 90 s according to the manufacturer's guidance. Next, the sample was exposed at the g-line (436 nm) for 20 s. The developing process was performed with a commercially-available photoresist developer (AZ 300 MIF, AZ electronic materials). To remove the revealed FPF, dry etching in ambient oxygen was conducted at an oxygen flow rate of 50 mL/min, a process pressure of 40 Pa, an RF-power of 100 W, and at a process time of 60 s.

Photoresist stripping was performed with a commercially-available photoresist stripper (AZ 400 T, AZ electronic materials), but the original solution of AZ 400 T was diluted with deionized water because the main solvent of AZ 400 T, N-methyl-2-pyrrolidone, dissolves the FPF. Details of the dilution ratio are described in our previous publication [15].

2.3. Double-coating of the ferroelectric polymer

Double-coating, in this work, means that a certain material was deposited by a solution-based process on the same material directly. Double-coating is possible if the solution for the ferroelectric polymer film coated secondly (the second FPF) does not dissolve the initially-coated ferroelectric polymer film (the first FPF). However, this successive solution-based deposition process cannot be applied to FPF as the first FPF is clearly affected by exposure to the solvent in the solution of the second FPF. Therefore, the solubility of the solution used for the second FPF needs to be controlled. According to the literature [16], the solubility of a solvent can be varied by mixing a portion of an insoluble solvent into the original soluble solvent on the principle that the