

Ferroelectric Polymer

FIELD OF THE INVENTION

The present invention relates to a ferroelectric polymeric film and a
5 method of fabricating a ferroelectric polymer.

BACKGROUND

Ferroelectric polymers are promising materials for electronic devices. For example, they are suitable for a non-volatile memory. Since a thin film can be
10 easily formed from a solution by means of a simple process such as spin-coating, die-coating, screen-printing or the other coating processes, the production cost of the devices utilizing a ferroelectric polymer is expected to be extremely cheap. However, remanence, which is the maximum spontaneous polarization when no external electric field is applied, of an organic material is generally lower than that
15 of an inorganic ferroelectric material. Remanence is one of most important properties for a ferroelectric material. When a ferroelectric material is used for a memory device, the magnitude of the output signal is proportional to its remanence. So there exists a strong demand of a ferroelectric material which has an improved remanence.

SUMMARY OF THE INVENTION

In general terms, one aspect of the invention proposes a ferroelectric polymer comprising Polyaminodifluoroborane (PADFB). This may have the advantage of increased remanence.

5 In a first specific expression of the invention there is provided a ferroelectric film as claimed in claim 1.

In a second specific expression of the invention there is provided a method of fabricating a ferroelectric polymer as claimed in claim 8.

10 In a third specific expression of the invention there is provided a ferroelectric solution as claimed in claim 12.

BRIEF DESCRIPTION OF THE DRAWINGS

One or more example embodiments of the invention will now be described, with reference to the following figures, in which:

Figure 1 is a molecular structure of PVDF.

15 Figure 2 is a molecular structure of PADBF.

Figure 3 is the relationship between remanence and concentration of PADFB.

Figure 4(a) is a device structure of 1T1C-type memory.

Figure 4(b) is a device structure of 1T-type memory.

20 Figure 4(c) is a device structure of cross point type memory

DETAILED DESCRIPTION

An example of a ferroelectric polymer is shown in Figure 1. The polyvinylidene fluoride (PVDF) molecule 100 includes H-C bonds 102 and F-C bonds 104. Ferroelectric properties of polymers may be related to the dipole moment induced between the hydrogen 106 and fluorine 108 atoms. This is also related to the polarity of the molecule.

A way to measure the dipole moment is by comparing the electronegativity of the atoms within the molecule. The electronegativity relates to the ability of an atom to attract electrons (or electron density) towards itself in a covalent bond. Since the electronegativity of fluorine atom is 4.0 and that of carbon is 2.5, the fluorine atom tends to be charged more negatively than the carbon atom in a F-C bond. On the other hand, hydrogen atom has only 2.2 in electronegativity. Therefore, the carbon atom tends to be charged more negatively than the hydrogen atom in an H-C bond. These properties induce imbalance of electron distribution, which leads to a strong dipole moment between the hydrogen and the fluorine atoms.

A further example of a ferroelectric polymer is shown in Figure 2. The polyaminodifluoroborane (PADFB) molecule 200 includes B-F bonds 202 and N-H bonds 204. The electronegativity of boron 206 is 2.0 and nitrogen 208 is 3.0, and therefore PADFB may have a dipole moment twice as large as PVDF due to the large differences of electronegativity in both B-F 202 and N-H 204 bonds. A larger dipole moment may have the advantage of higher remanence,

since remanence is proportional to the maximum dipole moment obtained when no external electric field is applied.

PADFB may be synthesised by pyrolysis of precursor (BF_3NH_3) and collected by a cold trap. Collected PADFB may be dissolved in
5 dimethylformamide (DMF) and spin-coated onto a glass substrate.

Since PADFB is a hygroscopic and brittle material, it may be difficult to obtain a continuous and air-stable film. It may be desirable to provide a ferroelectric polymer with improved phase separation, low hygroscopicity and/or improved film stability in air whilst still obtaining high remanence.

10 Certain ferroelectric polymers have improved film uniformity and stability. For example ferroelectric polymers such as P(VDF/TrFE), PVDF or Nylon11 may be more air stable and less hygroscopic than PADFB. According to the exemplary embodiment PADFB may be mixed with another material, for example a different ferroelectric polymer, to improve film uniformity and stability.

15 Figure 3 shows the remanence for a range of mixtures of P(VDF/TrFE) and PADFB. This shows that remanence increases when the concentration of PADFB is higher, since PADFB has higher remanence compared to P(VDF/TrFE). As shown in Figure 3, remanence tends to saturate between 10% and 20% in concentration of PADFB.

20 At least up until a concentration of 20%, most of PADFB molecules are surrounded by air-stable P(VDF/TrFE) molecules. Within this range the film was quite stable in air and significant absorption of water wasn't observed. A similar

effect was observed when PADFB was mixed with various ferroelectric polymers such as PVDF or Nylon11.

A mixture of PADFB and P(VDF/TrFE) may be produced by dissolving 8wt% of Dehydrated P(VDF/TrFE) pellets in dehydrated DMF in a glove box filled
5 with nitrogen gas, then dissolving 0.8 wt% of PADFB, in the solution. The solution may be an intermediate product. The solution can then be spin-coated on a glass substrate in the glove box to avoid absorption of water and annealed at 150°C for 3 hours. Alternatively for mass production a roll-to-roll process could be used where fabrication takes place on a running sheet-like substrate between two rolls
10 of the sheet. For example, a 10% PADFB concentration film produced as described above exhibits good remanence.

Using a high remanence ferroelectric polymer in memory devices may allow the device to be smaller or more information can be stored in the same area. Figures 4(a)-4(c) illustrate various structures of memory devices. The structure
15 shown in Fig. 4(a) is called 1T1C type which consists of a transistor 400 and a capacitor 402 having a ferroelectric polymer according to the exemplary embodiment as the dielectric. To write information in this memory cell, an electric field higher than the coerciveness of the ferroelectric material is applied between BL and PL while the transistor 400 is turned on by applying voltage to WL for
20 example 1.5 V which is sufficiently larger than the threshold level of the transistor. Depending on the polarity of the electric field between BL and PL, either data "0" or data "1" is stored in the ferroelectric layer. In a reading operation, a certain polarity of electric field is applied between BL and PL while the appropriate

voltage is applied to WL. If the stored polarization reverses, a displacement current flows between BL and PL. On the other hand, if no polarization reversal is induced, no displacement current flows between BL and PL. Therefore, by detecting the displacement current, the stored information can be determined as having "0" or "1".

Figure 4(b) is a schematic of 1T type memory cell. The writing operation for the 1T type memory cell is the same as for the 1T1C type. An electric field higher than the coerciveness of the ferroelectric material 404 according to the exemplary embodiment is applied between BL and PL while the transistor 406 is turned on by applying an appropriate voltage to WL. To read the stored information in the cell, voltage is applied to WL for example 1.5 V while a certain magnitude of electric field smaller than the coerciveness is applied between BL and PL. Since the current flow between BL and PL differs depending on the direction of the stored polarization, the stored information can be determined as having "0" or "1".

Figure 4(c) shows a structure of so-called cross point type memory. It consists of top electrodes 408, bottom electrodes 410 and a ferroelectric layer 412 according to the exemplary embodiment. Top 408 and bottom 410 electrodes form a matrix and the ferroelectric layer 412 is sandwiched by these electrodes. When a pair of top 408 and bottom 410 electrodes is selected and a voltage is applied between them for example 30 V, an electric field exceeding coerciveness is induced at the corresponding cross point. Thus, writing or reading operation is executed following the same principle as 1T1C.

Whilst exemplary embodiments of the invention have been described in detail, many variations are possible within the scope of the invention as will be clear to a skilled reader.

CLAIMS:

1. A ferroelectric film comprising polyaminodifluoroborane (PADFB).
2. The ferroelectric film as claimed in claim 1 further comprising a
5 ferroelectric polymer mixed with the PADFB, the ferroelectric polymer being
different to PADFB.
3. The ferroelectric film as claimed in claim 1 or claim 2 wherein the
ferroelectric polymer is selected from the group consisting of
10 Polyvinylidene fluoride (PVDF), copolymer of Polyvinylidene fluoride and
Trifluoroethylene (P(VDF/TrFE)) and Polyundecanoamide (Nylon11).
4. The ferroelectric film as claimed in any one of the preceding claims
wherein the concentration of the PADFB is between 2wt% and 20wt%
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5. A memory device comprising one or more capacitor-like memory cells,
each cell comprising a pair of electrodes, a ferroelectric film as claimed in any
one of claims 1 to 4 being located between the electrodes.
- 20 6. A memory device comprising one or more field effect transistors (FET),
each transistor having a gate insulator made of a ferroelectric film as claimed in
any one of claims 1 to 4.

7. A memory device as claimed in claim 5 further comprising a switching transistor configured to apply a voltage to one of the electrodes

8. A method of fabricating a ferroelectric polymer comprising mixing a
5 predetermined amount of PADFB with a solvent.

9. The method as claimed in claim 8 further comprising mixing a predetermined amount of another different ferroelectric polymer with the PADFB and the solvent.

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10. The method as claimed in claim 8 or claim 9 further comprising forming a film with the solution.

11. The method as claimed in claim 10 further comprising annealing the film.

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12. A ferroelectric solution comprising
polyaminodifluoroborane (PADFB), and
a solvent.

20 13. The ferroelectric solution as claimed in claim 12 further comprising a ferroelectric polymer mixed with the PADFB and the solvent, the ferroelectric polymer being different to PADFB.