



A FERROELECTRIC POLYMER MEMORY DEVICE

FIELD OF THE INVENTION

The present invention relates generally to memory devices, particularly though
5 not solely to a multi-stack ferroelectric polymer memory device and a method of
fabricating a ferroelectric polymer memory device.

BACKGROUND

Semiconductor memories may be either non volatile, read only memory (ROM)
10 or volatile, random access memory (RAM). It is known to configure ferroelectric memory
devices as non-volatile, meaning, the stored information in a non-volatile memory
remains unaffected even after the device power is cut off.

Most prior art ferroelectric memory devices are based on ceramics and
configured as thin film based field effect transistors (FET). These devices require very
15 high processing temperatures (usually over 600°C) and sophisticated fabrication
equipment.

Ferroelectric polymers, such as poly(vinylidene-difluoride) and its copolymers
require substantially low temperature and infrastructure to process. Thin film deposition
methods, using polymer solutions, have made it easier to realise the required thickness of
20 these polymers on substrates. For example spin coating has been widely described as a
coating technique to deposit thin polymer films. However, spin coating has certain
limitations, like its inability to be used in a continuous fabrication process, as well as it is
not suitable for coating large size substrates. Dip coating is another technique which can



be used to coat substrates, but the dip-coated thin films are often non-uniform in thickness.

Various configurations of a memory device with single layer of ferroelectric polymer (FEP) and fabrication methods have been disclosed. For example US patent 6756620 discloses the use of L-B deposited FEP layers to coat a spin coated FEP layer. The spin-on FEP layer is surface engineered, and damage at the interface between the FEP layer and the electrodes is reduced. US patent 6812509 discloses depositing a thin organic semiconductor (Polyphenylenes, thiophene oligomers, pentacene, polythiophene) film onto a FEP thin film before source and drain electrodes are deposited. A polymer dielectric layer (Polyimide, PVC, PMMA, PVDF, P(VDF-TrFE) in paraelectric state) may also be deposited between the FEP thin film and organic semiconductor film.

US patent 6624457 discloses fabrication of a multi-rank, stacked polymer memory device. However, the fabrication process involves repeated photolithography, and is highly complicated.

Similarly US patent 6858862 discloses a fabrication process which involves repeated photolithography.

Fabrication of the metallic electrodes is an important step in the memory device manufacturing. An additive technique to build the metallic electrodes may be desirable compared to subtractive photolithography.

US patent 6863936, for example, describes surface activation of polyimide film surface by laser irradiation, for electroless metal plating. US patent 5378508 discloses irradiating a laser beam on a metal-organic salt coated substrate to provide conductive metal deposit on the substrate.

It would therefore be desirable to provide multi-stack a ferroelectric polymer memory device which might provide improved performance. It would also be desirable, to provide a ferroelectric polymer memory device which could be easily adapted for roll-to-roll fabrication.

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SUMMARY OF THE INVENTION

It is therefore the objective of at least one embodiment to provide a ferroelectric polymer memory device or a method of fabricating a ferroelectric polymer memory device that overcomes at least one of the above-mentioned problems.

10 In accordance with a first aspect of the invention there is provided a ferroelectric polymer memory device having a plurality of overlapping stacks wherein each stack comprises a ferroelectric polymer thin film layer sandwiched between insulating and / or protective intermediate layers, and each intermediate layer incorporating an electrode array.

15 Each intermediate layer may surround each electrode array.

Each intermediate layer may be a polymer-metal organic composite thin film which is electrically insulating.

The electrode arrays may be arranged orthogonally about each ferroelectric layer to form a matrix of memory cells; each memory cell being formed between the
20 intersections of respective electrode arrays, and wherein each intermediate electrode array forms part of the immediately upper stack and the immediately lower stack.

The ferroelectric layer may be made of ferroelectric polymers such as poly(vinylidene-difluoride) PVDF or poly(vinylidene fluoride-trifluoroethylene) P(VDF-TrFE).

5 The memory device may further comprise a substrate of insulating polymer under the first electrode array.

The memory device may further comprise a protective layer of insulating polymer thin film on the last electrode array.

The memory device may further comprise microvias electrically connecting each electrode array.

10 In accordance with a second aspect of the invention there is provided a method of fabricating a ferroelectric polymer memory device comprising:

forming a first electrode array

forming a first ferroelectric layer on the first electrode array,

forming a intermediate layer on the first ferroelectric layer,

15 forming a second electrode array within and / or from portions of the intermediate layer,

forming a second ferroelectric layer on the intermediate layer and / or the electrode array, and

forming a third electrode array on the second ferroelectric layer.

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In accordance with a third aspect of the invention there is provided a method of fabricating a ferroelectric polymer memory device comprising:

forming a first intermediate layer,

forming a first electrode array within and / or from portions of the first intermediate layer,

forming a ferroelectric layer on the first intermediate layer and / or the first electrode array,

5 forming a second intermediate layer on the ferroelectric layer, and

forming a second electrode array within and / or from portions of the second intermediate layer.

One or more of the intermediate layers may be protective and / or insulating layers.

10 Forming one or more of the intermediate layers may comprise coating a metal organic composite polymer thin film by a continuous coating technique.

Forming one or more of the electrode arrays may comprise selectively laser irradiating the portions of the corresponding intermediate layer, the irradiated portions forming the electrode array.

15 Forming one or more of the ferroelectric layers may comprise coating a ferroelectric polymer thin film by a continuous coating technique.

The method may be repeated to fabricate a multi stack memory device.

The method may further comprise continuously coating an insulating polymer thin film onto the last electrode array and / or intermediate layer to form a protective layer.

20 The method may further comprise the step of forming microvias to each electrode array to provide electrical connections.

The continuous coating may be a process selected from one of the group of die, capillary, meniscus, spiral bar and doctor blade coating.

The laser irradiating may be Laser Induced Metallisation (LIM) or Laser Direct Writing (LDW).

The laser may be either pulsed laser or excimer laser and may have wavelength and power configured according to the characteristics of the intermediate layer.

5 The method may further comprise electroless plating one or more of the electrode arrays.

The method may further comprise forming the metal organic composite from a solution of a reactive monomer(s) and/or a reactive polymer(s), a metal organic compound and a solvent.

10 The reactive monomer(s) may be selected from one or more of the group of methyl methacrylate and styrene, the reactive polymer(s) may be selected from one or more of the group of epoxy, urethane and polyimide and the metal organic compound may be selected from one or more of the group of copper, aluminium, silver and gold linked with an organic molecule.

15 The method may further comprise either thermal or ultra-violet curing the polymer-metal organic composite film, to fabricate a cross linked composite film.

In accordance with a forth aspect of the invention there is provided a ferroelectric polymer memory device fabricated according to the method in any of the above paragraphs.

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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:

Figures 1(a) and 1 (b) are schematic drawings showing the construction of a multi-layer ferroelectric polymer memory device.

Figure 2 is a flow diagram of a method of fabrication of a ferroelectric polymer memory device.

5 Figures 3(a) to 3(j) are schematic drawings showing the steps of the method of fabrication in figure 2.

DETAILED DESCRIPTION

A first embodiment of the invention relates to a multi-stack ferroelectric polymer
10 memory device for storage applications. The device includes at least two stacks of ferroelectric polymer thin films sandwiched in between intermediate layers incorporating electrode arrays, supported on a polymer substrate. The non-volatile memory device is based on ferroelectric polymer thin film and may be completely polymeric using a polymeric substrate.

15 In a second embodiment of the invention a ferroelectric polymer memory device is fabricated according to a method which can be easily adapted for roll-to-roll device manufacturing.

The fabrication process may include laser-assisted techniques for selective metallization of the intermediate layers, to fabricate the metallic electrode arrays. Thus,
20 unlike conventional subtractive photolithographic techniques, additive techniques are used to pattern metallic features from a polymer composite. For example, Laser induced Metallisation (LIM) or Laser Direct Writing (LDW) with appropriate wavelength and

power may be used to form the metallic electrodes. Also the fabrication process may be a mask-less metal patterning process.

The intermediate layer which may include metal organic composite with an insulating polymer, may be formed onto the substrate or on the ferroelectric polymer film.

5 During the laser irradiation, the metal organic compound dissociates the metallic species and organic species. The metallic species, remain on the substrate / ferroelectric polymer and form the metallic electrode, whereas, the organic fumes or gases are released into the atmosphere. The un-irradiated portions of the intermediate layer remain insulating and act as a protective layer.

10 The fabrication process may also employ a continuous coating technique such as die, capillary, meniscus, spiral bar or doctor blade coating, to deposit highly uniform polymeric layers on the substrate. These coating methods allow depositing thin polymer film on the wide area of polymer substrates in a continuous process to achieve an even thickness. Spin, dip and spray coating may also be used.

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The multi-stack memory device

According to the first embodiment the ferroelectric polymer memory device comprises at least two stacks of ferroelectric polymer thin film sandwiched between intermediate layers and electrodes, supported on a substrate.

20 Figure 1 shows the ferroelectric polymer memory device 100, comprising three stacks 102, 104, 106 fabricated on substrate 108.

The substrate 108 is flexible, and it can be a thick sheet or a thin film in the physical form. It can be made of variety of polymeric materials which can sustain at least

150°C temperature, for example, polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polyimide and poly(vinylidene difluoride) (i.e. PVDF). The substrate is insulating and may in some applications be ferroelectric.

The first stack 102 comprises a first intermediate layer 112, a first electrode array 110 a first ferroelectric layer 114, a second electrode array 116 and a second intermediate layer 118. The first electrode array 110 lies on the upper surface of the substrate 108.

Each electrode 136 in the electrode array may be a strip of metal of various size and/or shape, depending on the application. For example the shape may be rectangular strips or L-shaped strips. The length of each electrode may be in the range of millimetre to few centimetres. The width of the electrode may be between 1µm to 200µm, for example 20µm. The thickness of each electrode may be between 10nm to 500nm, for example 100nm. The electrode array may be made of electrically conductive materials such as silver, copper, nickel, aluminium or gold. The electrode array may comprise between several tens to thousands of electrodes.

The first intermediate layer 112 covers the exposed surface of the substrate 108, between the individual electrodes 136. The intermediate layer is a thin polymeric film, for example, insulating and non-ferroelectric polymer, about the same thickness as the electrode array, and may be made of electrically insulating polymer.

On top of the first electrode array 110 and the first intermediate layer 112, is the first ferroelectric layer 114. The ferroelectric layer is a ferroelectric polymer thin film such as PVDF, P(VDF-TrFE) with a thickness about 100nm to 5µm, for example 500nm.

The second electrode array 116 lies on the first ferroelectric layer 114. The second electrode array 116 may be configured similarly to the first electrode array 110 but

arranged orthogonally to form a matrix of memory cells; each memory cell 138 being formed between the intersection of respective electrodes.

Similarly the second intermediate layer 118 covers the exposed surface of the first ferroelectric layer between the individual electrodes of the second electrode array 116. The second intermediate layer 118 is a thin polymeric film, about the same thickness as the second electrode array 116, and may for example be made of electrically insulating polymer.

The intermediate layers and their fabrication assist in the fabrication process. For example normally when a second ferroelectric layer is coated onto a first ferroelectric layer, the first ferroelectric layer may be damaged in the process.

According to the first embodiment the deposition of an intermediate layer should not cause damage or deterioration to the substrate or the ferroelectric layer underneath. The solvent used for the intermediate layer, should not dissolve the substrate or the ferroelectric layer underneath. The drying or curing conditions (temperature and duration) should not cause any damage or deterioration to the substrate or the ferroelectric layer underneath. The dried or cured (fully processed) intermediate layer remains unaffected after deposition of the next ferroelectric layer on top of it, eg: the solvent used for the next ferroelectric layer and the drying and annealing temperature cycles. Accordingly the intermediate layers may also be protective layers, where they provide protection from damage to the lower ferroelectric layers, as each new layer of ferroelectric polymer is coated onto the device.

Thus, as explained above, the sandwich structure of the first electrode array 110, the first intermediate layer 112, the first ferroelectric layer 114, the second intermediate

layer 118 and the second electrode array 116, form the first stack 102 of the memory device 100.

The second stack 104 comprises the second electrode array 116, the second intermediate layer 118, a second ferroelectric layer 120 a third intermediate layer 124 and
5 a third electrode array 122. The third intermediate layer 124 covers the exposed surface of the second ferroelectric layer 120, between the individual electrodes of the third electrode array 122.

Because, in a multi-stack arrangement, each intermediate layer, incorporating an intermediate electrode array, forms part of the immediately upper stack and the
10 immediately lower stack, the stacks may be termed overlapping. In case of a single stack device, the intermediate layers will simply be the layers either side of the ferroelectric layer.

The third stack 106 comprises the third electrode array 122, the third intermediate layer 124, a third ferroelectric layer 126, a forth intermediate layer 130 and a
15 forth electrode array 128. The forth intermediate layer 130 covers the exposed surface of the third ferroelectric layer 126, between the individual electrodes of the forth electrode array 128.

The forth electrode array 128 and forth intermediate layer 130 are covered with a protective layer 132 of insulating polymer. The individual electrodes of each of the
20 electrode arrays, are electrically connected by conductive micro-vias 134. These may be formed by either mechanical or laser drilling followed by metallising the vias to make then conductive.

Thus, the multi-stack memory device structure is fabricated by multiple ferroelectric layers, electrode arrays and intermediate layers. Thus in order to improve performance, any number of such stacks is theoretically feasible to fabricate.

5 **Fabrication of the memory device**

According to the second embodiment a method 200 of fabricating a memory device is shown in Figure 2. In step 202 a first intermediate layer is formed. In step 204 a first electrode array is formed within and / or from portions of the first intermediate layer. In step 206 a first ferroelectric layer is formed on the first intermediate layer and / or the first electrode array. In step 208 a second intermediate layer is formed on the first ferroelectric layer. In step 210 a second electrode array is formed within and / or from portions of the second intermediate layer.

Thus the first stack 102, or single stack device, may be fabricated according to steps 202 to 210. To fabricate a multi stack memory device the above steps may be repeated, as per steps 212 to 216.

In step 212 a second ferroelectric layer is formed on the second intermediate layer and / or the second electrode array. In step 214 a third intermediate layer is formed on the second ferroelectric layer. In step 216 a third electrode array is formed within and / or from portions of the third intermediate layer.

Alternatively the first electrode and last electrode in the stack, may be fabricated according to any method as is known in the art.

Each step of the method 200 will now be described in more detail with reference to Figure 3. In step 202 an insulating polymer thin film is continuously coated onto the substrate to fabricate the first intermediate layer, as shown in Figure 3(b).

Figure 3(a) shows the polymer substrate 108. Figure 3(b) shows the polymer
5 substrate 108 coated with a polymer-metal organic composite thin film to fabricate the first intermediate layer 112. A metal organic compound and a suitable insulating polymer(s) or monomer(s) are dissolved in a solvent. This solution is coated on the substrate by batch (e.g. spin coating or dip coating) or continuous coating techniques (for example die, capillary, meniscus, spiral bar, and doctor blade coating). The substrate and
10 first intermediate layer are then baked at 50-100°C to remove the solvent and polymerize or cross link the reactive monomer(s) or polymer(s), resulting in a polymer-metal organic composite thin film on the substrate. Photo assisted polymerization or curing of the reactive monomer(s) or polymer(s) can also be adapted to fabricate a cross linked polymer-metal organic composite thin film on the substrate, for example ultra-violet
15 curing.

The metal organic compound may be chosen from a wide range of compounds of metals such as copper, aluminium, silver, gold linked with an organic molecule, for example a molecule including oxygen.

Reactive monomers such as, various types of acrylic, or vinyl families, for
20 example methyl methacrylate or styrene, and reactive polymers such as from the families of epoxy, urethane, polyimide polymers and the like may be used, along with the metal organic compound to form a cross linked composite thin film.

In step 204 portions of the first intermediate layer are selectively laser irradiated, to fabricate the first electrode array, as shown in Figure 3(c).

Figure 3(c) shows the polymer-metal organic composite thin film 112, after being selectively irradiated by laser, to induce direct metal writing to fabricate the first electrode array 110. A laser beam is irradiated along the desired path (as per the required electrode shape) on the first intermediate layer 112. A laser beam is configured with appropriate wavelength, power, frequency, number of repetitions, velocity so that the polymer-metal organic composite selectively decomposes to form metallic species and organic species in the laser-irradiated regions, for example, pulsed laser or excimer laser. The decomposed organic species are released in the form of vapour or gas, whereas, the metallic species remains on the surface of the substrate, fabricating the first electrode array 110 thereon. The regions of the intermediate layer 112, which are not exposed to the laser, remain unaffected, to act as an insulator. The electrode array 110 may also be electroless plated with additional layer of metals, with suitable metals such as copper or nickel, to improve electrical conductivity.

Step 206 is shown in more detail in Figure 3(d). Figure 3(d) shows a thin film of ferroelectric polymer 114 coated on the top surface of the first electrode array 110 and the first intermediate layer 112. Polymers such as, PVDF, P(VDF-TrFE) and PVDCN, could be used as ferroelectric polymers. The ferroelectric layer may be manufactured by using the polymer solution in an appropriate solvent, such as dimethyl formamide (DMF), methyl-ethyl ketone (MEK). The solution is deposited by batch (e.g. spin coating or dip coating) or continuous coating techniques (for example die, capillary, meniscus, spiral bar,

and doctor blade coating). The device is then subjected to drying to remove the solvent, followed by an annealing step to improve the ferroelectric properties.

The annealing conditions may be varied depending on the materials used. For example, with P(VDF-TrFE) copolymer thin film, annealing at 150°C for 3 hours, followed by slow cooling, may provide good ferroelectric performance, in terms of remnant polarisation. Alternatively, annealing may be done at the end of the fabrication process.

In step 208 an insulating polymer thin film is coated onto the first ferroelectric layer to fabricate the second intermediate layer, as shown in Figure 3(e).

In Figure 3(e) the top surface of the first ferroelectric layer is coated with polymer-metal organic composite thin film to fabricate the second intermediate layer 118, similarly to step 202.

In step 210 portions of the second intermediate layer are selectively laser-irradiated to fabricate the second electrode array, as shown in Figure 3(f).

In Figure 3(f) the second intermediate layer 118 is subjected to laser-assisted direct writing of the second electrode array 116, similarly to step 204. The geometry and shapes of the individual electrodes of the second electrode array 116, are configured to form a matrix with all first electrode array 110. The un-irradiated region of the polymer-metal organic composite film remains as the intermediate layer 118 in between the electrodes.

Thus the first stack, or single stack 102 may be fabricated according to Figure 3(a) to 3(f). To fabricate a multi stack memory device the above steps may be repeated.

Step 212 is shown in Figure 3(g) where a second layer of ferroelectric polymer thin film coated on top of the second electrode array to fabricate a second ferroelectric layer 120.

Step 214 is shown in Figure 3(h) where the second ferroelectric layer 120 is
5 coated with polymer-metal organic composite thin film, to fabricate a third intermediate layer 124.

Step 216 is shown in Figure 3(i) where the third intermediate layer 124 is subjected to laser-assisted direct writing of a third electrode array. Again the geometry and shapes of the individual electrodes of the third electrode array 122, are configured to
10 form a matrix with the second electrode array 116.

Thus in Figures 3(g) to 3(i) the second stack 104 is fabricated.

In Figure 3(j) a protective layer 132 of an insulating polymer is coated on top to fabricate a 2 stack memory device. The device may be annealed at appropriate temperature and duration to improve the ferroelectric performance. Electrical connections
15 to each electrode are provided by micro vias 134.

One or more embodiments of the memory device and/or method of fabrication may allow at least reduced production cost over the prior art. This may allow application as a sheet like memory device for business cards, printing papers, identity cards, passports, and work permits with memory, or the like.

CLAIMS:

1. A ferroelectric polymer memory device having a plurality of overlapping stacks wherein each stack comprises a ferroelectric polymer thin film layer sandwiched between insulating and / or protective intermediate layers, and each intermediate layer
5 incorporating an electrode array.
2. The memory device as claimed in claim 1 wherein each intermediate layer surrounds each electrode array.
- 10 3. The memory device as claimed in claim 1 or claim 2 wherein each intermediate layer is a polymer-metal organic composite thin film which is electrically insulating.
4. The memory device as claimed in any one of the preceding claims wherein the electrode arrays are arranged orthogonally about each ferroelectric layer to form a matrix
15 of memory cells; each memory cell being formed between the intersections of respective electrode arrays, and wherein each intermediate electrode array forms part of the immediately upper stack and the immediately lower stack.
5. The memory device as claimed in any one of the preceding claims wherein the
20 ferroelectric layer is made of ferroelectric polymers such as, poly(vinylidene-difluoride) PVDF or poly(vinylidene fluoride-trifluoroethylene) P(VDF-TrFE).

6. The memory device as claimed in any one of the preceding claims further comprising a substrate of insulating polymer under the first electrode array.
7. The memory device as claimed in any one of the preceding claims further comprising a protective layer of insulating polymer thin film on the last electrode array.
8. The memory device as claimed in any one of the preceding claims further comprising microvias electrically connecting each electrode array.
9. A method of fabricating a ferroelectric polymer memory device comprising:
 - forming a first electrode array,
 - forming a first ferroelectric layer on the first electrode array,
 - forming an intermediate layer on the first ferroelectric layer,
 - forming a second electrode array within and / or from portions of the intermediate layer,
 - forming a second ferroelectric layer on the intermediate layer and / or the electrode array, and
 - forming a third electrode array on the second ferroelectric layer.
10. A method of fabricating a ferroelectric polymer memory device comprising:
 - forming a first intermediate layer,
 - forming a first electrode array within and / or from portions of the first intermediate layer,

forming a ferroelectric layer on the first intermediate layer and / or the first electrode array,

forming a second intermediate layer on the ferroelectric layer, and

forming a second electrode array within and / or from portions of the second
5 intermediate layer.

11. The method as claimed in claim 9 or claim 10 wherein one or more of the intermediate layers are protective and / or insulating layers.

10 12. The method as claimed in any one of claims 9 to 11 wherein forming one or more of the intermediate layers comprises coating a metal organic composite polymer thin film using a continuous coating technique.

13. The method as claimed in any one of claims 9 to 12 wherein forming one or
15 more of the electrode arrays comprises selectively laser irradiating the portions of the corresponding intermediate layer, the irradiated portions forming the electrode array.

14. The method as claimed in any one of claims 9 to 13 wherein forming one or more of the ferroelectric layers comprises coating a ferroelectric polymer thin film using a
20 continuous coating technique.

15. The method as claimed in any of claims 9 to 14 wherein the method is repeated to fabricate a multi stack memory device.

16. The method as claimed in any of claims 9 to 15 further comprising coating an insulating polymer thin film onto the last electrode array and / or intermediate layer to form a protective layer.

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17. The method as claimed in any of claims 9 to 16 further comprising the step of forming microvias to each electrode array to provide electrical connections.

18. The method as claimed in claim 12 or claim 14 wherein the continuous coating is a
10 process selected from one of the group of die, capillary, meniscus, spiral bar and doctor blade coating.

19. The method as claimed in claim 13 wherein the laser irradiating is laser induced metallization (LIM) or Laser Direct Writing (LDW).

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20. The method as claimed in claim 13 or claim 19 wherein the laser is pulsed laser or excimer laser with wavelength and power configured according to the characteristics of the intermediate layer.

20 21. The method as claimed in any of claims 9 to 20 further comprising electroless plating one or more of the electrode arrays.

22. The method as claimed in claim 12 further comprising forming the metal organic composite from a solution of a reactive monomer(s) and/or a reactive polymer(s), a metal organic compound and a solvent.

5 23. The method as claimed in claim 22 wherein the reactive monomer(s) is selected from one or more of the group of methyl methacrylate and styrene, the reactive polymer(s) is selected from one or more of the group of epoxy, urethane and polyimide and the metal organic compound is selected from one or more of the group of copper, aluminium, silver and gold linked with an organic molecule.

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24. The method as claimed in any one of claims 12, 22 or 23 further comprising thermal or ultra-violet curing the polymer-metal organic composite film, to fabricate a cross linked composite film.

15 25. A ferroelectric polymer memory device fabricated according to the method as claimed in any one of claims 9 to 24.