

# A Method For Forming A Piezoelectric Device

## Technical Field

The present invention generally relates to a method  
5 for forming a piezoelectric device. The present invention  
also relates to a piezoelectric device.

## Background

The energy harvested through the piezoelectric effect  
10 is now sufficient to power many electrical devices and  
wireless communications with rapidly progressive low power  
electronics. Strong demands for resource sustainability  
and maintaining a green environment are also promoting the  
quick expansion of applications in various energy  
15 harvesting and energy efficient technologies. According to  
a market forecast concerning autonomous devices (where the  
harvesting and the driven devices are no more than 1 meter  
apart), it is shown that the market for the harvesting  
elements will increase from 564.3 million in year 2010, to  
20 4090.3 million by year 2019. The overall market for the  
devices and systems employing these energy harvesting  
elements could be tens or even hundreds of times larger.

Currently the market-dominant piezoelectric materials  
for mechanical energy harvesting are ferroelectric ceramic  
25 materials. Piezoelectric polymers, such as poly(vinylidene  
fluoride) (PVDF)-based ferroelectric polymers, possess  
several desirable advantages for use in applications, such  
as low processing temperature, large area processing  
ability, high flexibility, low density and good mechanical  
30 impedance match. However, such piezoelectric polymers  
typically have substantially smaller piezoelectric  
coefficient, which limits their applications for energy  
harvesting. Multilayer structures made of piezoelectric

polymer materials have been proposed and fabricated to improve the harvested energy for applications.

There are several problems as described below in current methods of preparing piezoelectric polymer multilayer materials and their applications for energy harvesting.

For example, piezoelectric polymer multilayer materials are often fabricated by stacking and bonding multiple separated polymer sheets after electrode coating. However in this method, bonding of the individual sheets with adhesive agents is a complicated process, particularly when the thickness of the layers is reduced and the area of the polymer sheets is increased. A small thickness is often preferred for realizing an improved electrical impedance match and enhanced electrical energy output. This is particularly critical to piezoelectric polymers, which usually have extremely large impedance. Existence of the inactive adhesive layers also unfavorably affects the electrical output of the piezoelectric polymer multilayer materials due to the local clamping effect. Furthermore, after obtaining the polymer multilayer, extra processing steps need to be taken to connect the electrode layers coated on the individual sheets to form the two electrical terminals.

To obtain large electrical energy, it is desired that the piezoelectric polymer multilayer can work when mechanically bent. However, when the piezoelectric polymer multilayer materials are fabricated by the stacking and bonding process, an extra fabrication step is required to bond the piezoelectric polymer multilayer onto a flexible substrate for generating electrical energy through the mechanical bending.

Piezoelectric polymer multilayer materials can also be fabricated by alternately depositing thin layers of

piezoelectric polymer and electrode on a substrate. In this deposition approach, the piezoelectric polymer layers are deposited through a "thin film" process, such as by depositing the solution of the polymer on the substrate by spin-coating or dip-coating, or depositing the vapor of the polymer by sputtering or by an evaporation process. However, multiple cycles of large area vapor deposition to produce a polymer multilayer on a flexible substrate can get too expensive for energy harvesting applications. Further, repeated solution deposition to produce a piezoelectric polymer multilayer on a flexible substrate is difficult, as the exposure to the solvent in the subsequent coating will affect the prior coated layers. In addition, the piezoelectric polymer layers need to be patterned for the electrode connections, and there is a serious problem in reliably connecting the thin electrode layers between the polymer layers. It is also necessary to selectively remove or etch excess dielectric material to connect the electrode layers, thereby requiring an extra processing step to form the electrical terminals.

For piezoelectric PVDF-based polymers, expensive PVDF copolymers, such as P(VDF-TrFE), are used to produce a piezoelectric film and multilayer on a substrate. However, the low cost PVDF homopolymer cannot be used to fabricate the multilayer on a substrate because the deposited thin layers on the substrate are unable to go through a significant mechanical stretching process as required to convert the as-deposited piezoelectric-inactive PVDF  $\alpha$  phase to the piezoelectric-active ferroelectric  $\beta$  phase. Thus, PVDF homopolymer materials cannot be used to fabricate the multilayer on a flexible substrate at a reduced material cost.

There is therefore a need to provide an improved process for producing piezoelectric multilayer materials

that can overcome, or at least ameliorate, one or more of the disadvantages described above.

In addition, there is a need to provide a piezoelectric multilayer device that possesses enhanced electrical energy output.

#### Summary

According to a first aspect, there is provided a method for forming a piezoelectric device comprising the steps of:

- (a) depositing a first electrode;
- (b) depositing a piezoelectric material layer on the first electrode layer to thereby cover the first electrode layer while leaving a region of the first electrode layer uncovered;
- (c) depositing a second electrode layer on the piezoelectric material layer;
- (d) depositing a piezoelectric material layer on the second electrode layer to thereby cover the second electrode layer while leaving a region of the second electrode layer uncovered; and
- (e) repeating steps (a) to (c), and optionally step (d), to build multiple repeating first electrode layers separated from the second electrode layers by piezoelectric material layers, wherein all of the uncovered regions of the first electrode layers converge at a point A to integrally form a first electrode and all of the uncovered regions of the second electrode layers converge at a point B to integrally form a second electrode in which point A is displaced at a distance from point B.

Advantageously, the electrodes may be integrally formed as the piezoelectric device is being formed such that the process may exclude a step of connecting an

external electrode to the piezoelectric device. As such, the process may advantageously exclude an additional step of etching or cutting the piezoelectric material layers in order to connect the external electrode to the layers. The process may also exclude the step of using an adhesive to connect the external electrode to the piezoelectric device. In this way, the piezoelectric device formed by the disclosed process may not face problems of having the electrodes falling out once the adhesive loses its adhesion ability. In addition, the presence of the adhesive, which is usually electrically inactive, may lead to a local clamping effect which unfavourably affects the electrical output of the piezoelectric device.

Advantageously, the disclosed process may not require the step of spin-coating when depositing the piezoelectric material layers. Still advantageously, the disclosed process may not require the step of screen-printing when depositing the piezoelectric material layers. Hence, by avoiding the use of spin-coating or screen-printing, the piezoelectric material layers having a desired large area can be deposited. Impurities such as organic residue from the printing vehicle are not present.

Advantageously, a low cost piezoelectric homopolymer (such as poly(vinylidene fluoride) or PVDF) can be used in the disclosed process as an alternative to the more expensive PVDF-copolymer.

According to a second aspect, there is provided a piezoelectric device comprising a plurality of repeating layers having the following sequence:

- (a) a first electrode layer,
- (b) a piezoelectric material layer covering the first electrode layer while leaving a region of the first electrode layer uncovered,
- (c) a second electrode layer, and optionally

(d) a piezoelectric material layer covering the second electrode layer while leaving a region of the second electrode layer uncovered,

5 wherein all of the uncovered regions of the first electrode layers are connected together at a point A and all of the uncovered regions of the second electrode layers are connected together at a point B wherein point A is displaced at a distance from point B.

10 It is to be noted that at least two piezoelectric material layers are required to be present in the piezoelectric device.

Advantageously, the disclosed piezoelectric device may have a more reliable electrode connection as compared to prior art piezoelectric devices due to the direct  
15 connection of the various electrode layers with each other.

According to a third aspect, there is provided an energy storage device comprising the piezoelectric device as defined above. The energy storage device can work under  
20 mechanical bending mode such that when a mechanical force or acceleration is applied on the (flexible) substrate with the piezoelectric material multilayers, electricity can be generated due to the strain in the piezoelectric material multilayers through the piezoelectric effect.

25 According to a fourth aspect, there is provided a wafer of piezoelectric devices comprising:

a substrate; and

a plurality of piezoelectric devices as defined above disposed on the substrate.

30 Advantageously, this may allow the piezoelectric devices to be mass-produced at low cost. The individual piezoelectric devices can then be separated from each other by cutting or dicing the wafer.

## Definitions

The following words and terms used herein shall have the meaning indicated:

5 The term "piezoelectric", when used in conjunction with a material or a device, refers to the ability of the material or device to generate an electric charge when a pressure is applied onto the material or device.

10 The term "integrally formed" is to be interpreted broadly to refer to the direct connection between the respective electrode layers with each other to form the respective electrodes as the piezoelectric device is being formed such that the piezoelectric device and the electrodes can be deemed as a single connected unit. The piezoelectric device does not require additional etching  
15 or cutting steps in order to connect the electrodes to the device.

The term "connected together" when referring to the electrode layers, refers to the direct contact between the electrode layers without any intervening material in  
20 between.

The word "substantially" does not exclude "completely" e.g. a composition which is "substantially free" from Y may be completely free from Y. Where necessary, the word "substantially" may be omitted from  
25 the definition of the invention.

Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit  
30 inclusion of additional, unrecited elements.

As used herein, the term "about", in the context of concentrations of components of the formulations, typically means +/- 5% of the stated value, more typically +/- 4% of the stated value, more typically +/- 3% of the

stated value, more typically, +/- 2% of the stated value, even more typically +/- 1% of the stated value, and even more typically +/- 0.5% of the stated value.

Throughout this disclosure, certain embodiments may  
5 be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be  
10 considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4,  
15 from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

Certain embodiments may also be described broadly and  
20 generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the disclosure. This includes the generic description of the embodiments with a proviso or negative limitation removing any subject matter from the  
25 genus, regardless of whether or not the excised material is specifically recited herein.

#### **Detailed Disclosure of Embodiments**

Exemplary, non-limiting embodiments of a method for  
30 forming a piezoelectric device will now be disclosed.

The method comprises the steps of: (a) depositing a first electrode layer; (b) depositing a piezoelectric material layer on the first electrode layer to thereby cover the first electrode layer while leaving a region of

the first electrode layer uncovered; (c) depositing a second electrode layer on the piezoelectric material layer; (d) depositing a piezoelectric material layer on the second electrode layer to thereby cover the second electrode layer while leaving a region of the second electrode layer uncovered; and (e) repeating steps (a) to (c), and optionally step (d), to build multiple repeating first electrode layers separated from the second electrode layers by piezoelectric material layers, wherein all of the uncovered regions of the first electrode layers converge at a point A to integrally form a first electrode and all of the uncovered regions of the second electrode layers converge at a point B to integrally form a second electrode in which point A is displaced at a distance from point B.

The process may exclude the step of etching the piezoelectric material layers in order to connect an external electrode to the piezoelectric device.

The first electrode layer may be deposited on a substrate. The substrate may be made of a material that confers flexibility to the substrate. The substrate may be made of any flexible materials, including but not limited to, metal, alloy, polymer, composite. Aluminum is used here as an example. Other examples of flexible materials include, but are not limited to, high-carbon spring steel, stainless steel, titanium, beryllium copper and acetal copolymer.

The substrate may be cleaned with an organic solvent in order to prepare the surface for coating with the electrode layers and/or piezoelectric material layers. The organic solvent may be a ketone such as acetone or an alcohol such as isopropanol.

The process may comprise the step of depositing an insulating layer on the substrate. The insulating layer

may be deposited before the first electrode layer is deposited.

The insulating layer may comprise an organic polymer as an example. The organic polymer may be a ferroelectric polymer. The ferroelectric polymer may comprise monomers selected from the group consisting of vinyls, vinylidene halides, acrylonitriles, amides, fluoroethylenes, halides and combinations thereof. The ferroelectric polymer may be selected from the group consisting of polyvinylidene halides such as polyvinylidene fluorides (PVDF) and polyvinylidene chlorides, polyvinylidene fluoride trifluoroethylene (P(VDF-TrFE)), polyacrylonitriles, polyamides, copolymers and combinations thereof. In one embodiment, the ferroelectric polymer is PDVF. The PVDF homopolymer may be more cost effective than other piezoelectric materials. In another embodiment, the ferroelectric polymer is P(VDF-TrFE).

The insulating layer may be deposited on the substrate via dip-coating. The withdrawing speed during dip-coating may be about 20 mm/min to about 30 mm/min. The withdrawing speed may be about 25 mm/min. The thickness of the insulating layer may be selected from the range of about 5  $\mu\text{m}$  to about 15  $\mu\text{m}$ , about 5  $\mu\text{m}$  to about 6  $\mu\text{m}$ , about 5  $\mu\text{m}$  to about 8  $\mu\text{m}$ , about 5  $\mu\text{m}$  to about 10  $\mu\text{m}$ , about 5  $\mu\text{m}$  to about 12  $\mu\text{m}$ , about 5  $\mu\text{m}$  to about 14  $\mu\text{m}$ , about 6  $\mu\text{m}$  to about 15  $\mu\text{m}$ , about 8  $\mu\text{m}$  to about 15  $\mu\text{m}$ , about 10  $\mu\text{m}$  to about 15  $\mu\text{m}$ , about 12  $\mu\text{m}$  to about 15  $\mu\text{m}$  and about 14  $\mu\text{m}$  to about 15  $\mu\text{m}$ . In one embodiment, the thickness of the insulating layer may be about 10  $\mu\text{m}$ .

The insulating layer may be subjected to a heating and subsequent annealing step in order to improve the crystallinity of the polymer present in the insulating layer. The heating temperature, when P(VDF-TrFE) is used as the insulating layer, may be selected from the range of

about 80°C to about 120°C, or about 100°C. The annealing step may be carried out at a temperature in the range of about 130°C to about 140°C, or about 135°C.

5 The first and second electrode layers may be deposited via physical vapor deposition or chemical vapor deposition. The physical vapor deposition may comprise electron-beam evaporation and sputtering.

10 The first and second electrode layers may be deposited through a mask in order to form a desired pattern or shape on the substrate.

The first and second electrode layers may comprise a material independently selected from the group consisting of a metal, a conductive metal-oxide, alloys thereof, and combinations thereof. The metal may be a Group IIIA metal or a transition metal. The first and second electrode layers may be comprised of a different material or may be comprised of the same material. The first and second electrode layers may be independently selected from aluminium, nickel, copper, silver, gold, titanium, platinum, rhodium, iridium, ruthenium, palladium, from metals that form conductive metal oxides, such as  $\text{IrO}_x$ ,  $\text{RuO}_x$  and  $\text{RhO}_x$  (where  $x < 4$ ); from conductive oxides; and from alloys of any of those materials.

25 The first and second electrode layers may have a thickness independently selected from the range of about 0.05  $\mu\text{m}$  to about 1  $\mu\text{m}$ , about 0.05  $\mu\text{m}$  to about 0.1  $\mu\text{m}$ , about 0.05  $\mu\text{m}$  to about 0.2  $\mu\text{m}$ , about 0.05  $\mu\text{m}$  to about 0.3  $\mu\text{m}$ , about 0.05  $\mu\text{m}$  to about 0.4  $\mu\text{m}$ , about 0.05  $\mu\text{m}$  to about 0.5  $\mu\text{m}$ , about 0.05  $\mu\text{m}$  to about 0.6  $\mu\text{m}$ , about 0.05  $\mu\text{m}$  to about 0.7  $\mu\text{m}$ , about 0.05  $\mu\text{m}$  to about 0.8  $\mu\text{m}$ , about 0.05  $\mu\text{m}$  to about 0.9  $\mu\text{m}$ , about 0.1  $\mu\text{m}$  to about 1  $\mu\text{m}$ , about 0.2  $\mu\text{m}$  to about 1  $\mu\text{m}$ , about 0.3  $\mu\text{m}$  to about 1  $\mu\text{m}$ , about 0.4  $\mu\text{m}$  to about 1  $\mu\text{m}$ , about 0.5  $\mu\text{m}$  to about 1  $\mu\text{m}$ , about 0.6  $\mu\text{m}$  to

about 1  $\mu\text{m}$ , about 0.7  $\mu\text{m}$  to about 1  $\mu\text{m}$ , about 0.8  $\mu\text{m}$  to about 1  $\mu\text{m}$  and about 0.9  $\mu\text{m}$  to about 1  $\mu\text{m}$ .

The process may comprise the step of depositing the piezoelectric material layers. The depositing step may  
5 comprise the step of dip coating. The depositing step may comprise the step of spray coating or casting. The withdrawing speed during the dip coating may be about 10 mm/min to about 20 mm/min, or about 15 mm/min.

The piezoelectric material layers may be deposited on  
10 the respective electrode layers to cover the respective electrode layers while leaving a region of the respective electrode layers uncovered. This can be carried out by leaving the electrode regions (which is defined by the uncovered regions) out of the piezoelectric material  
15 dipping solution. Hence, the electrode regions can be exposed for contact with the other electrode regions of the subsequently deposited electrode layers of the same group. The uncovered region of the various electrode layers will then converge at a point in order to form the  
20 respective electrodes for the piezoelectric device.

The piezoelectric material layer may comprise the same material as the insulating layer. Hence, the piezoelectric material layer may comprise an organic polymer. The organic polymer may be a ferroelectric  
25 polymer. The ferroelectric polymer may comprise monomers selected from the group consisting of vinyls, vinylidene halides, acrylonitriles, amides, fluoroethylenes, halides and combinations thereof. The ferroelectric polymer may be selected from the group consisting of polyvinylidene  
30 halides such as polyvinylidene fluorides (PVDF) and polyvinylidene chlorides, polyvinylidene fluoride trifluoroethylene (P(VDF-TrFE)), polyacrylonitriles, polyamides, copolymers and combinations thereof. In one embodiment, the ferroelectric polymer is PDVF. In another

embodiment, the ferroelectric polymer is P(VDF-TrFE). The P(VDF-TrFE) may be in admixture with a hydrated salt such as, for example, hydrated aluminium nitrate or  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ .

5       The thickness of each individual piezoelectric material layer may be selected from the range of about 2  $\mu\text{m}$  to about 30  $\mu\text{m}$ , about 2  $\mu\text{m}$  to about 5  $\mu\text{m}$ , about 2  $\mu\text{m}$  to about 10  $\mu\text{m}$ , about 2  $\mu\text{m}$  to about 15  $\mu\text{m}$ , about 2  $\mu\text{m}$  to about 20  $\mu\text{m}$ , about 2  $\mu\text{m}$  to about 25  $\mu\text{m}$ , about 25  $\mu\text{m}$  to  
10   about 30  $\mu\text{m}$ , about 20  $\mu\text{m}$  to about 30  $\mu\text{m}$ , about 15  $\mu\text{m}$  to about 30  $\mu\text{m}$ , about 10  $\mu\text{m}$  to about 30  $\mu\text{m}$  and about 5  $\mu\text{m}$  to about 30  $\mu\text{m}$ . The thickness of the piezoelectric material layer may be about 25  $\mu\text{m}$ . In order to achieve the desired thickness of the piezoelectric material layer, a second  
15   dip-coating step may be carried out.

After each deposition of the piezoelectric material layer, the device may be subjected to a heating step in order to improve the crystallinity of the piezoelectric material layer. The piezoelectric property of the  
20   piezoelectric material layer may be improved by increasing the crystallinity of the polymer present in the piezoelectric material layer. For piezoelectric P(VDF-TrFE) layer, the heating step may be carried out at a temperature selected from the range of about 130°C to about  
25   140°C, or about 135°C.

There is also provided a piezoelectric device comprising a plurality of repeating layers having the following sequence:

- (a) a first electrode layer,
- 30   (b) a piezoelectric material layer covering the first electrode layer while leaving a region of the first electrode layer uncovered,
- (c) a second electrode layer, and optionally

(d) a piezoelectric material layer covering the second electrode layer while leaving a region of the second electrode layer uncovered,

wherein all of the uncovered regions of the first electrode layers are connected together at a point A and all of the uncovered regions of the second electrode layers are connected together at a point B wherein point A is displaced at a distance from point B.

It is to be noted that at least two piezoelectric material layers are required to be present in the piezoelectric device. The piezoelectric device may be formed from the process disclosed herein.

The first and second electrode layers may comprise a material independently selected from a metal, a conductive metal-oxide, alloys thereof, and combinations thereof. The metal may be a Group IIIA metal or a transition metal. The first and second electrode layers may be comprised of a different material or may be comprised of the same material. The first and second electrode layers may be independently selected from aluminium, nickel, copper, silver, gold, titanium, platinum, rhodium, iridium, ruthenium, palladium, from metals that form conductive metal oxides, such as  $\text{IrO}_x$ ,  $\text{RuO}_x$  and  $\text{RhO}_x$  (where  $x < 4$ ); from conductive oxides; and from alloys of any of those materials.

The first and second electrode layers may have a thickness independently selected from the range of about 0.05  $\mu\text{m}$  to about 1  $\mu\text{m}$ , about 0.05  $\mu\text{m}$  to about 0.1  $\mu\text{m}$ , about 0.05  $\mu\text{m}$  to about 0.2  $\mu\text{m}$ , about 0.05  $\mu\text{m}$  to about 0.3  $\mu\text{m}$ , about 0.05  $\mu\text{m}$  to about 0.4  $\mu\text{m}$ , about 0.05  $\mu\text{m}$  to about 0.5  $\mu\text{m}$ , about 0.05  $\mu\text{m}$  to about 0.6  $\mu\text{m}$ , about 0.05  $\mu\text{m}$  to about 0.7  $\mu\text{m}$ , about 0.05  $\mu\text{m}$  to about 0.8  $\mu\text{m}$ , about 0.05  $\mu\text{m}$  to about 0.9  $\mu\text{m}$ , about 0.1  $\mu\text{m}$  to about 1  $\mu\text{m}$ , about 0.2  $\mu\text{m}$  to about 1  $\mu\text{m}$ , about 0.3  $\mu\text{m}$  to about 1  $\mu\text{m}$ , about 0.4  $\mu\text{m}$  to

about 1  $\mu\text{m}$ , about 0.5  $\mu\text{m}$  to about 1  $\mu\text{m}$ , about 0.6  $\mu\text{m}$  to about 1  $\mu\text{m}$ , about 0.7  $\mu\text{m}$  to about 1  $\mu\text{m}$ , about 0.8  $\mu\text{m}$  to about 1  $\mu\text{m}$  and about 0.9  $\mu\text{m}$  to about 1  $\mu\text{m}$ . The thickness of the first and/or second electrode may be about 0.2  $\mu\text{m}$ .

5 The thickness of the first and/or second electrode may be about 0.3  $\mu\text{m}$ .

The piezoelectric material layer may comprise an organic polymer. The organic polymer may be a ferroelectric polymer. The ferroelectric polymer may  
10 comprise monomers selected from the group consisting of vinyls, vinylidene halides, acrylonitriles, amides, fluoroethylenes, halides and combinations thereof. The ferroelectric polymer may be selected from the group consisting of polyvinylidene halides such as  
15 polyvinylidene fluorides (PVDF) and polyvinylidene chlorides, polyvinylidene fluoride trifluoroethylene (P(VDF-TrFE)), polyacrylonitriles, polyamides, copolymers and combinations thereof. In one embodiment, the ferroelectric polymer is PDVDF. In another embodiment, the  
20 ferroelectric polymer is P(VDF-TrFE).

The thickness of each individual piezoelectric material layer may be selected from the range of about 2  $\mu\text{m}$  to about 30  $\mu\text{m}$ , about 2  $\mu\text{m}$  to about 5  $\mu\text{m}$ , about 2  $\mu\text{m}$  to about 10  $\mu\text{m}$ , about 2  $\mu\text{m}$  to about 15  $\mu\text{m}$ , about 2  $\mu\text{m}$  to  
25 about 20  $\mu\text{m}$ , about 2  $\mu\text{m}$  to about 25  $\mu\text{m}$ , about 25  $\mu\text{m}$  to about 30  $\mu\text{m}$ , about 20  $\mu\text{m}$  to about 30  $\mu\text{m}$ , about 15  $\mu\text{m}$  to about 30  $\mu\text{m}$ , about 10  $\mu\text{m}$  to about 30  $\mu\text{m}$  and about 5  $\mu\text{m}$  to about 30  $\mu\text{m}$ . The thickness of the piezoelectric material layer may be about 25  $\mu\text{m}$ .

30 The thickness ratio of the piezoelectric material layer to the respective electrode layer may be more than 20, more than 50 or may be more than 100.

There is also provided an energy storage device comprising the piezoelectric device as disclosed above.

The energy storage device may be an energy harvesting device. The energy storage device may have an improved impedance match and enhanced electrical energy output as compared to other energy storage devices formed from the prior art processes. In the energy storage device, electricity can be generated due to the strain in the piezoelectric material multilayer as a result of a mechanical force or acceleration applied onto the piezoelectric device through the piezoelectric effect.

There is also provided a wafer of piezoelectric devices comprising:

a substrate; and

a plurality of piezoelectric devices as disclosed above disposed on said substrate.

By forming a plurality of piezoelectric devices on the wafer, the piezoelectric devices can be mass-produced easily on the industrial scale. The individual piezoelectric devices can then be separated from each other by cutting or dicing up the wafer.

#### Brief Description Of Drawings

The accompanying drawings illustrate a disclosed embodiment and serves to explain the principles of the disclosed embodiment. It is to be understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of the limits of the invention.

Fig. 1(a) shows the plan view of a starting flexible substrate 102 used in Example 1 and Fig. 1(b) shows the corresponding cross-sectional view of the substrate 102 along line AA'.

Fig. 1(c) shows the plan view of the substrate 102 used in Example 1 with the insulating layer 104 and Fig.

1(d) shows the corresponding cross-sectional view along line AA'.

Fig. 1(e) shows the plan view of a first electrode layer 106 (of a first block of repeating multi-layers) formed on the substrate 102 in Example 1 and Fig. 1(f) shows the corresponding cross-sectional view along line AA'.

Fig. 1(g) shows the plan view of the first active piezoelectric layer 108 (of the first block of repeating multi-layers) formed on the sample in Example 1 and Fig. 1(h) shows the corresponding cross-sectional view along line AA'.

Fig. 1(i) shows the plan view of the sample after the deposition of the second electrode layer 110 (of the first block of repeating multi-layers) in Example 1 and Fig. 1(j) shows the corresponding cross-sectional view along line AA'.

Fig. 1(k) shows the plan view of the second active piezoelectric layer 112 (of the first block of repeating multi-layers) formed on the sample in Example 1 and Fig. 1(l) shows the corresponding cross-sectional view along line AA'.

Fig. 1(m) shows the plan view of a first electrode layer 114 (of a second block of repeating multi-layers) in contact with the first electrode layer 106 (of the first block of repeating multi-layers) in Example 1 and Fig. 1(n) shows the corresponding cross-sectional view along line AA'.

Fig. 1(o) shows the plan view of a second electrode layer 118 (of the second block of repeating multi-layers) in contact with the second electrode layer 110 (of the first block of repeating multi-layers) in Example 1 and

Fig. 1(p) shows the corresponding cross-sectional view along line BB'.

Fig. 1(q) shows a schematic diagram of the plan view of all of the first electrode layers of the sample obtained in Example 1 and Fig. 1(r) shows the  
5 corresponding cross-sectional view along line AA'.

Fig. 1(s) shows a schematic diagram of the plan view of all of the second electrode layers of the sample obtained in Example 1 and Fig. 1(t) shows the  
10 corresponding cross-sectional view along line BB'.

Fig. 2 shows a schematic diagram of the electric connection during the poling process used in Example 1.

Fig. 3 shows a graph of voltage and energy against time of the experimental values from Example 1  
15 superimposed with simulated values of voltage and energy.

Fig. 4(a) shows the cross-sectional view of the cantilever beam 300 used in Example 1 and Fig. 4(b) shows the top view of the cantilever beam 300.

Fig. 5 shows a graph of voltage and energy against  
20 time of the simulated measurements of the open circuit voltage and energy generated in Example 2.

Fig. 6 shows a graph of peak voltage and energy against number of layers obtained in Example 3.

Fig. 7 shows a graph of energy output against load  
25 resistance of the 22-layer P(VDF-TrFE) piezoelectric polymer multilayer material and the single layer P(VDF-TrFE) polymer material used in Example 4.

Fig. 8(a) shows a schematic diagram of the plan view of the array of multiple elements obtained in Example 5  
30 and Fig. 8(b) shows the corresponding cross-sectional view along line CC'.

Figs. 9(a) and 9(b) show a schematic diagram of the two shadow masks used to produce the first and second electrode layers respectively in Example 5.

In the figures, like numerals denote like parts.

5

### Examples

Non-limiting examples of the invention and comparative examples will be further described in greater detail by reference to specific Examples, which should not  
10 be construed as in any way limiting the scope of the invention.

#### Example 1

**Fabrication of a piezoelectric polymer material on a  
15 flexible substrate**

The method used in this example for fabricating a piezoelectric polymer material on a flexible substrate is described in Figs. 1(a) to 1(t).

In this example, a 0.5 mm-thick aluminium sheet, was  
20 used as a starting flexible substrate 102. The plan view of the flexible substrate 102 used is shown in Fig. 1(a), while the cross-sectional view of the substrate 102 along line AA' is shown in Fig. 1(b). Prior to coating the piezoelectric polymer onto the aluminium sheet, the  
25 surface of the aluminium sheet was cleaned with acetone and isopropanol.

Thereafter, the piezoelectric polymer precursor solution was prepared for the subsequent dip-coating deposition process. The piezoelectric polymer precursor  
30 solution was prepared by dissolving poly(vinylidene fluoride-trifluoroethylene) P(VDF-TrFE) (70/30 mole ratio) in a solvent methyl ethyl ketone (20% by weight). An

automated dip coater was then used for the P(VDF-TrFE) dip-coating process, by withdrawing the aluminium substrate at a controlled withdrawing speed of 25 mm/min from the P(VDF-TrFE) solution. This yielded a film with a thickness of around 10  $\mu\text{m}$ . The sample was then heated on a hotplate at 100°C and subsequently annealed at 135°C in an oven to improve the crystallinity of the P(VDF-TrFE) layer.

The P(VDF-TrFE) layer also serves as an insulating layer on the aluminium substrate before the subsequent coating of any electrode layers. The plan view of the substrate 102 with the insulating layer 104 is shown in Fig. 1(c), while the cross-sectional view along line AA' is shown in Fig. 1(d).

An aluminium electrode layer with a thickness between 0.05  $\mu\text{m}$  to 1  $\mu\text{m}$  was then deposited by conventional electron-beam evaporation to form the first electrode layer 106 (of the first block of repeating multi-layers) (denoted hereinafter as "first<sub>1</sub>"). The plan view of the first<sub>1</sub> layer 106 formed on the substrate is shown in Fig. 1(e), while the cross-sectional view along line AA' is shown in Fig. 1(f). This first<sub>1</sub> layer 106 had a pattern with an extended part 107 like a finger formed through a shadow mask during the evaporation.

The deposition of the first<sub>1</sub> layer 106 was then followed by the dip coating of a first P(VDF-TrFE) active layer 108, which is the first active piezoelectric layer. The sample was dip coated to a controlled depth in the P(VDF-TrFE) solution and withdrawn at a speed of 15 mm/min. The depth was controlled so that the extended part of the first<sub>1</sub> layer 107 was exposed for the contact to subsequent first electrode layers. The plan view of the first active piezoelectric layer 108 is shown in Fig.

1(g), while the cross-sectional view along line AA' is shown in Fig. 1(h). As shown in Figs. 1(g) and 1(h), the polymer layer 108 as coated did not completely cover the odd<sub>1</sub> layer 106, leaving the extended part 107 uncovered.

5        The sample was then heated on a hotplate for 100°C. Another dip coating cycle could be carried out in order to increase the thickness of the first active P(VDF-TrFE) layer to approximately 25 μm. The samples were then annealed in an oven at 135°C to increase the crystallinity  
10      of the P(VDF-TrFE).

To build the piezoelectric multilayer materials, the electrodes were alternately deposited to sandwich the piezoelectric layers. In addition, the deposited electrodes alternate between the first and second  
15      electrode layers, which would form the two electrical terminals. Thus, the next electrode layer to be deposited by aluminium evaporation would be a second electrode layer (of the first block of repeating multi-layers) (denoted hereinafter as "second<sub>1</sub>"). Figs. 1(i) and 1(j) show the  
20      plan view and cross-sectional view along line AA' respectively of the sample after the deposition of the second<sub>1</sub> layer 110. As shown in Fig. 1(i), the second<sub>1</sub> layer 110 had a pattern with another extended part 111, as formed through another shadow mask during the evaporation  
25      process. The extended part 111 in the second<sub>1</sub> layer 110 was located at the same direction with the extended part 107 in the first<sub>1</sub> layer 106, but not overlapped with each other. Hence, the extended part 111 of the second<sub>1</sub> layer 110 (which is also arbitrarily defined as "point B") is  
30      displaced at a distance from the extended part 107 in the first<sub>1</sub> layer 106 (which is also arbitrarily defined as "point A").

Thereafter, a second P(VDF-TrFE) active layer 112 was coated thereon. The plan view of the second active piezoelectric layer 112 is shown in Fig. 1(k), while the cross-sectional view along line AA' is shown in Fig. 1(l).

5        After the dip-coating of the second P(VDF-TrFE) active layer 112, a first electrode layer (of a second block of repeating multi-layers) (denoted hereinafter as "first<sub>2</sub>") 114 was deposited by evaporation at about the same location of the first<sub>1</sub> layer 106 with the same shape.  
10    The plan view of the deposited first<sub>2</sub> layer 114 in contact with the first<sub>1</sub> layer 106 is shown in Fig. 1(m), while the cross-sectional view along line AA' is shown in Fig. 1(n). That is, the first<sub>2</sub> layer 114 also had an extended part 115 at about the same location as the extended part 107 of the  
15    first<sub>1</sub> layer 106. Thus, all of the "first" electrode layers (first<sub>1</sub> layer 106 and first<sub>2</sub> layer 114) were contacted at the extended parts uncovered by the P(VDF-TrFE) active layer 112.

Similarly, after coating of a third P(VDF-TrFE)  
20    active layer 116, a second electrode layer (of a second block of repeating multi-layers) (denoted hereinafter as "second<sub>2</sub>") 118 was deposited by evaporation thereon in contact with the second<sub>1</sub> layer 110 at the extended parts uncovered by the P(VDF-TrFE) active layers. The plan view  
25    of the deposited second<sub>2</sub> layer 118 in contact with the second<sub>1</sub> layer 110 is shown in Fig. 1(o), while the cross-sectional view along line BB' is shown in Fig. 1(p). That is, the second<sub>2</sub> layer 118 also had an extended part 119 at about the same location as the extended part 111 of the  
30    second<sub>1</sub> layer 110, wherein the extended parts 111 and 119 were uncovered.

With the continued process of coating the P(VDF-TrFE) active layer followed by the first electrode layer

(first<sub>n</sub>), and then coating the P(VDF-TrFE) active layer followed by the second electrode layer (second<sub>n</sub>), a sample with 5 layers of P(VDF-TrFE) polymer material and 6 electrode layers (3 "first electrode layers" and 3 "second electrode layers") was obtained. Hence, multiple repeating layers of the first electrode layer separated from the second electrode layers by piezoelectric layers are obtained.

A schematic diagram of the plan view of all of the "first electrode layers" is shown in Fig. 1(q), while the cross-sectional view along line AA' is shown in Fig. 1(r). Similarly, a schematic diagram of the plan view of all of the "second electrode layers" is shown in Fig. 1(s), while the cross-sectional view along line BB' is shown in Fig. 1(t). Hence, the uncovered regions of all of the "first electrode layers" converge at a point A and all of the uncovered regions of the "second electrode layers" converge at a point B, in which point A is displaced at a distance from point B.

By having all the "first electrode layers" converge at a point (A), a first electrode was integrally formed from all of the "first electrode layers". Similarly, by having all the "second electrode layers" converge at a point (B), a second electrode was integrally formed from all of the "second electrode layers". Hence, the first electrode and second electrode are formed at the same time of forming the piezoelectric device.

By repeating the process, repeating multilayers of first electrode layer, piezoelectric material layer, second electrode layer and optionally another piezoelectric material layer can be obtained on the flexible aluminium substrate 102. It is to be noted from Figs. 1(a) to 1(t) that all of the first electrode layers

converge at a point that is displaced at a distance from the point of convergence of all of the second electrode layers.

5 The P(VDF-TrFE) polymer multilayer material as fabricated above was electrically poled to have piezoelectric properties. A schematic diagram of the electric connection during the poling process used in this example is shown in Fig. 2.

10 In this process, a DC voltage was applied over the second electrode and the first electrode. The voltage was slowly increased to reach a field of  $40 \text{ V}/\mu\text{m}$ , at a temperature of  $100^\circ\text{C}$ , where the field was held at that value for 5 min.

15 The aluminium substrate for this experiment was  $4.3 \text{ cm} \times 1.8 \text{ cm} \times 0.5 \text{ mm}$ , and the various electrode layers were  $1 \text{ cm}$  by  $1 \text{ cm}$ .

The capacitance measured showed good agreement with the calculated values on the basis of the number of layers. Specifically, the measured capacitance of the 5  
20 P(VDF-TrFE) polymer layers was  $2.29 \text{ nF}$ , while the calculated value was  $2.38 \text{ nF}$ .

After poling, the voltage output was measured by clamping the sample at one end and deflecting the free end of the sample by  $5 \text{ mm}$ .

25 Specifically, a cantilever beam 300 was formed when one end of the flexible aluminium substrate 102 with the piezoelectric polymer multilayer material 302 alternating with the electrode layers 304 was clamped while the other end was free, as shown in Fig. 4. In particular, Fig. 4(a)  
30 shows the cross-sectional view of the cantilever beam 300, while Fig. 4(b) shows the top view of the cantilever beam 300. A force  $F$  is applied on the free tip of the

cantilevered beam 300 and subsequently the force  $F$  is removed, resulting in the bending vibration of the beam 300. Due to the piezoelectric effect, the piezoelectric polymer multilayer material 302 can convert the vibration  
5 energy into electric energy.

Fig. 3 presents the experimental voltage and energy measured from the bending vibrations of the cantilever beam 300 with an electrometer, superimposed with the simulated voltage and energy. Fig. 3 proves that the  
10 experimental and the simulated results show good agreement. Referring to Fig. 3, the initial voltage increase (indicated by arrow 202) was resulted from the depression of the cantilever tip, increasing to a maximum value of 15.5 V. The tip was then held down momentarily,  
15 resulting in the relatively flat portion of the voltage curve between 0.49 s and 0.76 s. After the tip was released, the vibration of the cantilever was excited and the energy generated was about 2.2  $\mu\text{J}$  (indicated by arrow 204).

20

### Example 2

In this example, a simulation of the poling process of Example 1 was repeated, except that the sample used was a 22-layer P(VDF-TrFE) polymer multilayer on the aluminium  
25 substrate, instead of a 5-layered P(VDF-TrFE) polymer multilayer on the aluminium substrate.

The thickness of each polymer layer was 20  $\mu\text{m}$ , and the thickness of each aluminium electrode layer was 1  $\mu\text{m}$ . The tip displacement was set as 7 mm.

30 The simulated measurements of the open circuit voltage and energy generated are shown in Fig. 5. Referring to Fig. 5, it can be seen that the peak voltage

is about 15.5 V and the electric energy generated is around 118  $\mu$ J. This evidences that the generated energy is sufficient to power many electronic devices, including radio frequency (RF) transmitters.

5

### Example 3

For a flexible cantilever beam with piezoelectric polymer multilayer material, the output energy and voltage will increase with the increase in layer number under the constant tip displacement condition.

10

In this example, it was found that the effect of the thickness of the electrode layer became more significant with an increased number of layers. The tip displacement was set as 7 mm.

15

Fig. 6 shows that a thick electrode layer will lead to substantially decreased energy generation when the number of layers is large. Thus, this proves that a piezoelectric polymer multilayer with thinner electrode layers as deposited by evaporation will have substantially improved energy output, in comparison to those with thicker electrodes, particularly when the number of layers is large.

20

### Example 4

25

In this example, two cantilever energy harvesters of the same dimensions as shown in Fig. 4 were used. The first comprised of a multilayer material of 22 layers of P(VDF-TrFE) (with a layer thickness of 20  $\mu$ m each) and 23 layers of aluminum electrodes (with a layer thickness of 1  $\mu$ m each). The other comprised one single layer of P(VDF-TrFE) having a thickness of 461  $\mu$ m and two aluminium electrode layers having a thickness of 1  $\mu$ m each.

30

Each of the two energy harvesters was connected to a load resistance. Fig. 7 shows the energy output from the 22-layer P(VDF-TrFE) piezoelectric polymer multilayer material and the single layer P(VDF-TrFE) polymer to the load resistance ranging from 25  $\Omega$  to 100 k $\Omega$ . It was found that the energy output of the 22-layer piezoelectric polymer multilayer was about 5 to 400 times higher than that of single layer piezoelectric polymer with the load resistance ranging from 25  $\Omega$  to 100 k $\Omega$ . This result evidences the significant advantage of the piezoelectric polymer multilayer material in energy harvesting for practical load applications compared to single layer piezoelectric polymer due to the improved impedance match.

#### Example 5

In this example, the fabrication process of producing one element described in Example 1 was used here to produce a plurality of elements of the piezoelectric polymer multilayer on a single flexible substrate.

The plan view of the array of multiple elements obtained is shown in Fig. 8(a), while the cross-sectional view along line CC' is shown in Fig. 8(b).

The electrode layers 304 for the array of the elements of the piezoelectric polymer multilayer material 302 was deposited with two shadow masks as shown in Figs. 9(a) and 9(b) for the first and second electrode layers, respectively.

After the fabrication of the piezoelectric multilayer elements array, individual piezoelectric multilayer elements can be separated by cutting across the substrate together with the piezoelectric polymer layer, such as by mechanical cutting, laser cutting, etc.

### Example 6

In this example, low cost poly(vinylidene fluoride) (PVDF) homopolymer was used to replace poly(vinylidene fluoride-trifluoroethylene) P(VDF-TrFE) copolymer as described in Example 1.

For producing PVDF multilayer elements on a flexible substrate, a solvent for PVDF can be prepared at room temperature by mixing dimethylformamide (DMF) and acetone (50:50 in volume). Aluminum nitrate nonahydrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) (8% by weight in PVDF) was added to the solvent solution to promote crystallization of the piezoelectric  $\beta$  phase in the resulting PVDF polymer.

After the  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was dissolved completely, the PVDF polymer was introduced to the above solvent solution and the resultant solution was stirred at 60°C for 40 minutes until a clear PVDF solution was obtained as a precursor solution.

The PVDF solution was dip-coated through multiple cycles on the flexible aluminium substrate, and the first and second electrode layers was alternately deposited as described in Example 1 to produce the PVDF multilayer material. To enhance the crystallization, the film was annealed at a temperature between 130-145°C. During annealing, the hydrate salt  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  dehydrated completely and was decomposed.

After electric poling, piezoelectric PVDF polymer multilayer material was produced on the flexible aluminium substrate.

30

### Comparative Example 1

#### Fabrication of a piezoelectric polymer multilayer material by spin-coating

Piezoelectric polymer multilayers on flexible  
5 substrates were fabricated by a spin coating process,  
instead of the dip-coating deposition process described in  
Example 1.

P(VDF-TrFE) was dissolved in a suitable solvent such  
as methyl-ethyl-ketone (MEK). The P(VDF-TrFE) solution was  
10 then applied to a flexible substrate by spin-coating  
deposition.

Next, the as-deposited film was annealed at 120°C for  
3 hours. The aluminium electrode was then formed on the  
P(VDF-TrFE) layer by evaporation through a shadow mask.  
15 The spin coating and electrode evaporation cycle was  
repeated to form P(VDF-TrFE) multilayers with alternate  
electrode layers.

To connect the electrode layers, various methods to  
expose the electrode layers were attempted, such as by  
20 mechanical cutting/dicing or laser-cutting the multiple  
piezoelectric polymer layers, dissolving the polymers with  
a solvent or removing the polymer by plasma etching. The  
exposed electrodes were then electrically connected  
together by conductive epoxy or other adhesive, or by Al  
25 or Au deposition in vacuum chambers.

#### *Problems of fabricating piezoelectric polymer multilayer by spin coating*

The fabrication of piezoelectric polymer multilayer  
30 by the spin-coating process typically gave unreliable  
results. One of the problems was the difficulty in  
preparing thick P(VDF-TrFE) film in one spin-coating

cycle. The ability to fabricate sufficiently thick P(VDF-TrFE) was required to produce a piezoelectric energy harvester with sufficient output voltage and to prevent electrical shorting and arcing across the P(VDF-TrFE) layer during poling. Spin-coating could typically produce uniform P(VDF-TrFE) films of only up to about 3  $\mu\text{m}$  in thickness over a relatively large area. For thicker P(VDF-TrFE) layers, the thickness uniformity of the P(VDF-TrFE) film across a substrate was very poor because very slow spin speed and/or high concentration/viscosity P(VDF-TrFE) solution were required.

Another problem with the fabrication of piezoelectric polymer multilayers by spin-coating process was the difficulty in electrically connecting the very thin (0.05 to 1  $\mu\text{m}$ ) electrode layers together. Cutting or dicing of the multiple piezoelectric polymer layers resulted in smearing of the P(VDF-TrFE) across the electrode surface and thus poor electrical contact with the external current collector layer (such as the conductive epoxy/adhesive and metal layer) used to join the internal aluminium electrode layers. Dissolving P(VDF-TrFE) with a solution was also unsatisfactory with irregular regions dissolved as the solvent was driven into the sample by capillary action. The subsequent drying also left a thin, non-conducting P(VDF-TrFE) layer which interfered with the joining of the electrode layers. In addition, connecting the exposed electrode layers by an external current collector layer was also unsatisfactory as the electrical contacts between the aluminum electrodes and conductive external current collector were often broken after the temperature cycling during poling. Selective removal of the P(VDF-TrFE) layer by plasma etching could possibly improve the exposure of the internal electrode layer. However, the contact with external current collector was still poor. In addition,

large area and deep dry etching requires expensive equipment and consumables, and is very time consuming for fabricating polymer multilayer structure.

Hence, by using dip coating instead of spin coating  
5 to deposit the piezoelectric multilayers, the above disadvantages can be substantially prevented or minimized.

## Comparative Example 2

### 10 Fabrication of a piezoelectric polymer multilayer material by screen-printing

Attempts were made to fabricate the P(VDF-TrFE)  
polymer multilayer using the screen-printing method.

In this process, 25% by weight of freeze-milled  
P(VDF-TrFE) polymer powder was mixed with organic vehicle  
15 ESL400 using a mortar and pestle for at least 20 minutes  
until a uniform paste was obtained. A patterned silver  
electrode was first deposited on flexible aluminium  
substrates with an insulating layer by screen printing  
with low temperature silver paste through a stainless  
20 steel screen. Then the P(VDF-TrFE) film was deposited by  
the screen-printing process on the silver electrode layer  
on the aluminium substrate, and dried at 145°C for 10 min.  
The printing process of P(VDF-TrFE) was repeated for three  
times until the desired thickness of 30  $\mu\text{m}$  was achieved.  
25 After the P(VDF-TrFE) film was dried at 145°C in a vacuum  
oven for 60 min, another silver electrode layer was  
printed on the film as a top electrode.

Although the screen-printing method did produce a  
working P(VDF-TrFE) single layer on the flexible aluminium  
30 substrate, short-circuiting was often observed and the  
yield was extremely low when multilayers were produced. In  
addition, organic residue from the printing vehicle

existed in the screen-printed P(VDF-TrFE) film, which also had a detrimental effect on the performance properties.

Hence, by using dip coating instead of screen printing to deposit the piezoelectric multilayers, the  
5 above disadvantages can be substantially prevented or minimized.

### Applications

The piezoelectric device may be used as an energy  
10 storage device or an energy harvester device.

The disclosed process may not require the use of adhesive agents to bond the individual layers together. In addition, the disclosed process may not require extra processing steps to connect the electrode layers coated on  
15 the individual sheets to form the two electrical terminals. The disclosed process may not require multiple cycles of large area polymer vapor deposition. The disclosed process may not require an additional etching or patterning step in order to form the electrical terminals.  
20 Hence, the disclosed process may be carried out with lesser number of steps as compared to prior art processes, which result in a more reliable piezoelectric multilayer through a process that is less complicated, uses simpler equipments and more cost effective.

25 It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such  
30 modifications and adaptations come within the scope of the appended claims.

## Claims

1. A method for forming a piezoelectric device comprising the steps of:

- 5 (a) depositing a first electrode layer;
- (b) depositing a piezoelectric material layer on said first electrode layer to thereby cover said first electrode layer while leaving a region of said first electrode layer uncovered;
- 10 (c) depositing a second electrode layer on said piezoelectric material layer;
- (d) depositing a piezoelectric material layer on said second electrode layer to thereby cover said second electrode layer while leaving a region of said second electrode layer uncovered; and
- 15 (e) repeating steps (a) to (c), and optionally step (d), to build multiple repeating first electrode layers separated from the second electrode layers by piezoelectric material layers, wherein all of the uncovered regions of said first electrode layers
- 20 converge at a point A to integrally form a first electrode and all of the uncovered regions of said second electrode layers converge at a point B to integrally form a second electrode, in which point A is
- 25 displaced at a distance from point B.

2. The method according to claim 1, further comprising the step of heating the substrate after each piezoelectric material layer depositing step to thereby

30 improve the piezoelectric property of the piezoelectric material layer.

3. The method according to claim 1 or claim 2, wherein said first and second electrode layers are deposited via vapor deposition.

5 4. The method according to claim 3, wherein said vapor deposition is physical vapor deposition.

10 5. The method according to claim 4, wherein said physical vapor deposition comprises electron-beam evaporation.

15 6. The method according to any one of the preceding claims, wherein said first and second electrode layers are deposited through a mask.

7. The method according to any one of the preceding claims, wherein said first and second electrode layers independently comprise a metal.

20 8. The method according to claim 7, wherein said first and second electrode layers are comprised of aluminium.

25 9. The method according to any one of the preceding claims, wherein the step of depositing the piezoelectric layers comprises the step of dip coating.

30 10. The method according to any one of the preceding claims, wherein said piezoelectric material layers comprise an organic polymer.

11. The method according to claim 10, wherein said organic polymer is a ferroelectric polymer.

12. The method according to claim 11, wherein said ferroelectric polymer comprises monomers selected from the group consisting of vinyls, vinylidene halides, acrylonitriles, amides, fluoroethylenes, halides and combinations thereof.

13. The method according to claim 11 or claim 12, wherein said ferroelectric polymer is PVDF-based polymer.

14. The method according to any one of claims 11 to 13, wherein said ferroelectric polymer is poly(vinylidene fluoride and trifluoroethylene).

15. The method according to claim 13, wherein said PVDF-based polymer is PVDF homopolymer in admixture with a hydrated salt.

16. A piezoelectric device comprising a plurality of repeating layers having the following sequence:

- (a) a first electrode layer,
- (b) a piezoelectric material layer covering said first electrode layer while leaving a region of said first electrode layer uncovered,
- (c) a second electrode layer, and optionally
- (d) a piezoelectric material layer covering said second electrode layer while leaving a region of said second electrode layer uncovered,

wherein all of the uncovered regions of said first electrode layers are connected together at a point A and all of the uncovered regions of said second electrode layers are connected together at a point B wherein point A is displaced at a distance from point B.

17. The piezoelectric device according to claim 16, wherein said first electrode layer is deposited on a substrate made of a flexible material.

5        18. The piezoelectric device according to claim 16 or claim 17, wherein said first and second electrode layers independently comprise a metal.

10       19. The piezoelectric device according to any one of claims 16 to 18, wherein said piezoelectric material layers comprise an organic polymer.

20. The piezoelectric device according to claim 19, wherein said organic polymer is a ferroelectric polymer.

15

21. The piezoelectric device according to claim 20, wherein said ferroelectric polymer comprises monomers selected from the group consisting of vinyls, vinylidene halides, acrylonitriles, amides, fluoroethylenes, halides and combinations thereof.

20

22. The piezoelectric device according to any one of claims 16 to 21, wherein the thickness of said first and second electrode layers are individually selected from the range of 0.05  $\mu\text{m}$  to 1  $\mu\text{m}$ .

25

23. The piezoelectric device according to any one of claims 16 to 22, wherein the thickness of said piezoelectric material layers are individually selected from the range of 2  $\mu\text{m}$  to 30  $\mu\text{m}$ .

30

24. The piezoelectric device according to any one of claims 18 to 23, wherein the thickness ratio of the

piezoelectric material layer to the respective electrode layer is more than 20.

25. The piezoelectric device according to claim 24,  
5 wherein the thickness ratio of the piezoelectric material layer to the respective electrode layer is more than 50.

26. An energy storage device comprising the piezoelectric device according to any one of claims 16 to  
10 25.

27. A wafer of piezoelectric devices comprising:  
a substrate; and  
a plurality of piezoelectric devices according to  
15 any one of claims 16 to 25 disposed on said substrate.