A review of flexible perovskite oxide ferroelectric films and their application

Wenxiu Gao a, Yi Zhu a, Yaojin Wang a, Guoliang Yuan a,*, Jun-Ming Liu b

a School of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing, 210094, China
b Laboratory of Solid State Microstructure and Innovation Center of Advanced Microstructures, Nanjing University, Nanjing, 210093, China

A R T I C L E   I N F O

Article history:
Received 27 September 2019
Accepted 2 November 2019
Available online 5 November 2019

Keywords:
Perovskite oxides
Flexible devices
Sensors
Energy harvesters
Memories

A B S T R A C T

Many perovskite oxide ferroelectrics (e.g. PbZr1-xTixO3, BaTiO3, LiNbO3) are born with multitudinous robust performances and have been widely used in sensors, actuators, surface acoustic wave devices, and memories et al. However, their hardness, brittleness and harsh synthesis conditions (i.e. high temperature and oxygen ambience) restrain their application into flexible electronic devices which are significant components among the three pillars of modern society development, i.e. energy, information and materials. Here we review the preparation of flexible devices based on these oxide ferroelectrics, including transferring these freestanding films to flexible substrates after separating ferroelectric oxide films from the hard substrates, such as Si and SrTiO3 crystals, and also direct fabrication methods without transferring process. Subsequently, we summarize three kinds of representative flexible devices, i.e. flexible ferroelectric memories, sensors and generators. These inorganic electronics not only show excellent electric properties competitive with those corresponding electronics on hard substrates but also exhibit good flexibility similar to many organic flexible electronics.

© 2019 The Chinese Ceramic Society. Production and hosting by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

Perovskite oxides are emerged as a significant class of materials on account of the abundant fascinating physical properties, earning its intensive research popularity in condensed matter physics and a wealth of practical device applications [1,2]. Classic perovskite oxides, among many functional materials, manifest a wide range of application functions that are closely linked with people’s life [3]. The widespread use of high-performance perovskites in memories, sensors, microelectronics, piezoelectric actuators, energy harvesting and storage systems, mechanical processing, ultrasonic energy converters as well as optical and other related devices have been occupied the application market [4].
As one of the typical and mature applications of perovskite oxides, ferroelectric memory devices benefit from the remnant polarization ($P_r$) of perovskites ferroelectrics, such as the memories based on bismuth lanthanum titanate (Bi$_{3.25}$La$_{0.75}$Ti$_3$O$_{12}$) and bismuth ferrite (BiFeO$_3$) [5–9]. Besides, lead zirconate titanate (Pb(Zr$_1$, XTi$_0$)$_3$O$_9$) series materials are widely used in medical B-ultrasound, ship’s sonar, machine tool positioning, dishwasher, reversing radar, other kinds of sensors as well as the precision positioning equipment closely related to production and life due to their excellent direct and inverse piezoelectric effects [10]. It is the excellent piezoelectricity, ferroelectricity, pyroelectricity, non-linear dielectric behavior, multiferroic properties, high ferroelectric Curie temperature and extremely strong stability. In a word, perovskite oxide ferroelectrics are widely used in high-end manufacturing industry, electronics industry and even those in social lives at present [11].

With the development of artificial intelligence & internet of things as well as the burgeoning diversified demand in human daily life, the electronic devices are required to be more flexible, compact and even transparent [12–14]. The generation of these flexible electronic devices has nevertheless put forward new requirements to the bendability of perovskite oxides with the evolution of modern science and technology. High-performance of perovskite oxides can definitely satisfy the applied demand for flexible electronic devices [15]. Apple inc. has been developing stylish, lightweight, flexible wearable electronics, such as wearable watches and flexible bracelets. Others are looking to integrate ferroelectric oxide films into small flexible wearable devices, including eyeglasses and eardrops, or 3D printing. What is worth mentioning is that medical self-powered pacemakers and timely medical sensors act as the emerging research focus in flexible wearable field. The flexible electronic devices, therefore, turn into the mainstream characters in the next generation (see Fig. 1).

Each component of flexible electronics, including substrates, functional films, and conductive electrodes, should be flexible, lightweight and stable [13,14,16–18]. In order to prepare the flexible memories, sensors and nano-generators, polyimide, polyethylene terephthalate (PET) and other polymers are often chosen as flexible substrates, and ferroelectric polymers such as poly(vanillylene fluoride-co-trifluoroethylene) (i.e. P(VDF-TrFE)) films are commonly used as functional layers [18–22]. These flexible electronics have been prepared on organic substrates at or near room temperature [23]. However, most organic sensors and memories show poor comprehensive performances in comparison with the commercial inorganic memories nowadays. Proverbially, the traditional perovskite oxides, being most of the functional ceramics, are inflexible, with high brittleness and strong rigidity, imposing the bottleneck and challenge in applying to flexible electric devices [24,25]. As a result, applying and improving the properties of perovskite oxides in flexible memories, flexible sensors, and flexible energy management (generation and storage) devices have become an emerging research hot-topic [26].

In this review, we focus on the flexible electronics based on perovskite oxide films. At first, the popular methods to prepare flexible or even freestanding oxide films to achieve flexible electronics are summarized. Subsequently, flexible ferroelectric memories, flexible sensors, and energy harvesters on the basis of piezoelectric effect are introduced. Finally, outlooks for the design and preparation of the high-quality flexible perovskite oxide electronics are given.

2. Preparation of flexible electronics with perovskite oxide

Perovskite compounds possess a lot of intriguing structural properties. The structurally distorted variations, such as octahedra distortion, cation displacements within the octahedra, and octahedra tilting, often occur with lower space group symmetry [27,28]. These distortions cause B cation electronic instabilities to relieve, which can further come to many unique physical properties, including high ferroelectric/ferromagnetic polarization and piezoelectric coefficients, high dielectric, as well as interesting optical and electrical properties. As shown in Fig. 2, the displacement of B-
site Ti in TiO$_6$ octahedra of BaTiO$_3$ is related to the electronic instability, whose resultant ferroelectricity is widely used in electronic ceramics industries [29]. As a result, perovskite oxides are characterized by a wide range of unique electronic, magnetic and optical technological applications.

Most perovskite oxide ferroelectric crystals or ceramics are too hard and brittle to be used in flexible electronics. Besides, their films are commonly grown on hard SrTiO$_3$, LaAlO$_3$, Si, and other rigid substrates with $>0.1$ mm in thickness at $>500$ °C in oxygen ambience, and thus these films also suffer from the brittleness and rigidity features and could not be as flexible as organic materials [30]. As shown in Fig. 3, the strain of the film ($\delta$) in the bending radius ($r$) can be roughly estimated according to $\delta \approx (h_1 + h_2)/r$, where $h_1$ and $h_2$ stand for the thickness of thin film and substrates, respectively [31,32]. If these hard substrates are separated from oxide films or $h_2$ is reduced to the orders of $\mu$m-scale, the films should be flexible enough to satisfy the requirements of flexible electronics and wearable apparatuses [26]. We will summarize six popular methods to prepare flexible oxide films and their electronics in the following paragraphs.

Like organic or molecular ferroelectric films [33], the composite composed of organic matrix (e.g. P(VDF-TrFE), Polydimethylsiloxane (PDMS)) and oxide ferroelectric particles (such as BaTiO$_3$, PbZr$_{1-x}$Ti$_x$O$_3$) can be directly grown on flexible organic substrate near room temperature [34–43], which is named as Method 1 here. For example, Chang Kyu Jeong et al. developed the flexible hybrid nanocomposite generator device, consisting of BaTiO$_3$ nanowires and P(VDF-TrFE) matrix between two electrodes on a flexible polyethylene terephthalate (PET) sheet. The synthesized BaTiO$_3$ nanowires were blended in a P(VDF-TrFE) (PVDF/PTrFE = 70/30 mol%) solution to make the nanocomposite generator. The mixture fluid was spin-casted on an indium–tin oxide (ITO)-coated PET substrate, followed by drying and annealing the piezoelectric copolymer. A Ti/Au top electrode was directly deposited on the nanocomposite layer and then subsequently poled using Cu wires.

Ferroelectric oxide films can be prepared on hard Si substrate, separated from Si substrate through etching and then transferred onto organic substrate to prepare flexible electronics [44–47], which is named as Method 2 here. For example, Fig. 4 shows a schematic of the fabrication steps of flexible Au/BaTiO$_3$/Pt nanogenerator [45]. At first, the Au/BaTiO$_3$ films were grown on a rigid Pt/Ti/SiO$_2$/Si substrate. Secondly, the Au/BaTiO$_3$/Pt structure was vertically etched using a mask with a narrow bridge pattern. Thirdly, anisotropic wet etching with 5% tetramethylammonium hydroxide removed the underlying Si layer and separated the Au/BaTiO$_3$/Pt structure ribbons from the mother substrates. Fourthly, a polydimethylsiloxane (PDMS) stamp was coated on the freestanding Au/BaTiO$_3$/Pt structures and then they were transferred onto PDMS through quick removing Si wafer. Fifthly, the structures were then placed on a polyurethane (PU)-coated plastic substrate, and then they were well settled on a plastic substrate when the PDMS was peeled away by ultraviolet illumination. Sixthly, the epoxy was spin-coated on top of Au/BaTiO$_3$/Pt/PU/plastic substrates and the metal contact area was then opened with a standard photolithography process.

Ferroelectric oxide film can be grown on the hard sapphire substrate, separated from the substrate by laser vaporing the film interface and then transferred onto the organic substrates to prepare flexible electronics [48], which is named as Method 3 here. For
example, Fig. 5 shows the schematic illustration of the fabrication steps of flexible and large-area PbZr0.52Ti0.48O3 thin film nanogenerator using the laser lift-off process. The PbZr0.52Ti0.48O3 thin film was deposited on a double-side polished sapphire substrate by sol-gel method with the highest annealing temperature of 650 °C. The PbZr0.52Ti0.48O3 on a sapphire substrate was then placed on the flexible PET substrate coated with ultraviolet sensitive as an adhesive. A beam of a XeCl excimer laser with a photon energy of 4.03 eV illuminated the backside of sapphire substrates to vaporize the interface between the PbZr0.52Ti0.48O3 layer (Eg = 3.2–3.6 eV) and the sapphire substrate. Then, the PbZr0.52Ti0.48O3 thin film was separated from the bulk sapphire and then transferred onto PET substrates. Next, interdigital electrodes were deposited onto PbZr0.52Ti0.48O3 thin films. To encapsulate the piezoelectric nanogenerator, epoxy was coated and followed by the patterned process to secure a contact area using a standard photolithography method.

ABO3 epitaxial film can be grown on the hard SrTiO3 substrate, separated by etching sacrificial layer (e.g. La0.7Sr0.3MnO3, Sr3Al2O6) and then transferred onto the organic substrate to prepare flexible electronics [49,50], which is named as Method 4 here. For example, Fig. 6a-c illustrates the process of complex perovskite oxide films integration on the flexible substrate. The (001) SrRuO3/Pb(Zr0.2Ti0.8)O3/SrRuO3 sandwich capacitor was grown on the thin La0.7Sr0.3MnO3 coated SrTiO3 substrate by using pulsed laser deposition (PLD) method. The La0.7Sr0.3MnO3 layer was selectively wet etched in a diluted KI + HCl solution to separate the SrRuO3/Pb(Zr0.2Ti0.8)O3/SrRuO3 capacitor which had been coated with polymethyl methacrylate (PMMA) as a transfer stamp. The capacitor was subsequently transferred onto a 10-nm Pt coated PET polymethyl methacrylate (PMMA) as a transfer stamp. The capac-

The oxygen ambience, which is named as Method 5 here [53–60]. For example, Sung Sik Won et al. prepared PbZr0.52Ti0.48O3 film on an ultra-thin Ni-Cr based austenitic steel metal foil substrate with sol-gel method at 650 °C [53]. Furthermore, Jie Jiang et al. present the realization of epitaxial PZT films on mica for flexible electronics (Fig. 7) [57]. The mica substrate has the advantages of atomically smooth surface, high thermal stability (Tm – 1000 °C), chemical inertness, high transparency, mechanical flexibility, and compatibility with present fabrication methods. This two-dimensional layered material can be mechanically exfoliated like graphene down to few tens of micrometers. Direct growth of functional oxides (29–32) on mica via the van der Waals epitaxy has been demonstrated recently in view of flexible device applications. This approach does not impose requirements of overcoming the issue of lattice mismatch between the film and substrate that results in a significant reduction of defect density. Moreover, a weak van der Waals interaction between the film and substrate can further reduce the substrate clamping effect, favoring better device performance [26]. Fig. 7 shows the design and an actual flexible nonvolatile memory based on mica/(111) SrRuO3/(111)
PbZr0.52Ti0.48O3 structure. These memories not only retain the superior properties of epitaxial films but also exhibit mechanical flexibility, durability, and thermal stability.

High-quality piezoelectric single crystal can be reduced to μm-scale in thickness and mounted on flexible organic substrate (such as PET) to achieve flexible electronics, which is named as Method 6 here [61 Hwang GT, 62 Kim DH, and 63 Hwang GT]. For example, Geon-Tae Hwang et al. chosen Pb(Mg1/3Nb2/3)O3-PbTiO3 (PMN-PT) and Pb(112/Nb12/3)O3-Pb(Mg1/3Nb2/3)O3-PbTiO3 (PIN-PMN-PT) single crystals with the piezoelectric $d_{33}$ coefficient of over 2500 pC/N to prepare energy harvester. Commonly, the single crystal was bonded on a hard substrate (e.g. glass or Si) with an adhesive wax and then it was polished to an μm-scale thick film. After top metal electrodes were grown on film surface near room temperature, the film was fixed on an organic substrate (e.g. PET) with an adhesive epoxy (e.g. PU). Then, the sample was heated at the melting point of the adhesive wax to separate the hard substrate from the single-crystal film. Finally, the top interdigitated electrodes were deposited on the single-crystal film on the organic substrate.

3. Flexible ferroelectric memories

The storage mechanism of ferroelectric random access memory (FRAM) is rendered by the electrically switchable ferroelectric polarization, two ferroelectric polarization states corresponding to storage “0” and “1”, resulting from the positive and negative remnant polarization ($P_r$). The stored data, therefore, is kept from losing during power failure, accomplishing the effects for nonvolatile memory [64]. FeRAM possesses inherent superior fast speed performance, high information density, unlimited write-read cycles property, wide operating temperature range, and the qualification of serving in harsh environment, there acting as a part of portable IC cards or even radiation resistance aerospace equipment [65,66].

The achievement of flexible ferroelectric perovskite oxides in memory devices is fruitful, and as a result, it meets the appearing requirement in growing development of flexible electronic systems, which are able to be bent or under complex shaped infrastructures with different stresses, intactly [44,67]. Besides, their small-scale design provides them with both portability and lightweight in most cases. These flexible memory devices are essential parts of E-paper, wearable computers, flexible displays and other complex-shaped infrastructures, which has been increasingly emphatically cited in recent years. Here, we summarize several flexible ferroelectric non-volatile random access memories [68].

Adhering the mechanism of ferroelectric memory device material demands low deposition temperature, high $P_r$ value, low coercive field ($E_C$), and high anti-fatigue property with low leakage current, and PbZr0.8Ti0.2O3 is the most popular candidate among the most common ferroelectric perovskite oxides for flexible ferroelectric memory devices. PbZr0.35Ti0.65O3 ribbons were combined with patterned graphene to set up a non-volatile ferroelectric memory device, mounted flexibly on the Polyimide (PI) substrate. The $P_r$ was 30 μC/cm² and the memory window was 6V [46]. It is robust after 200 times bending cycles with the small bending radius of 9 mm. Besides, the polycrystalline PbZr0.52Ti0.48O3 was fabricated on a mica substrate with Pt and Au electrodes. The high-performance ferroelectricity remained as $P_r$ ~30 μC/cm² and 10⁸ polarization switching cycles. Its smallest bending degree was with the radius of 2 mm which can undergo 10¹ times repeated bending-releasing cycles as well [69].

PbZr0.8Ti0.2O3, due to its high remnant polarization, low coercive electric field and low crystallization temperature, is another exemplification that overcomes the daunting challenge and enables the high-performance utilization in flexible ferroelectric memory devices [70]. Ghoneim et al. prepared the flexible memory device with polycrystalline PbZr0.52Ti0.48O3 film which could be bent to 1.25 cm radius and showed a 35% degradation of $P_r$ after polarization switching up to 10⁶ cycles at room temperature [71]. It operated normally with the temperature increasing from 20 °C to

Fig. 7. Flexible perovskite oxide films directly grown on mica. Growth scheme (a) and photob (b) of flexible oxide films on mica. (c) Atomic force micrograph. (d) Schematic illustration of PbZr0.35Ti0.65O3/mica heterostructure via van der Waals heteroepitaxy. Reprinted with permission from ref 57. Copyright 2019, Rights Managed by American Association for the Advancement of Science.
225 °C, which can be explained by the composition and crystallization conditions of the ferroelectric oxide [72,73]. Furthermore, the <001> oriented single crystal complex oxide SrRuO3/PbZr0.2Ti0.8O3 films were grown on the rigid SrTiO3 substrates and then transferred onto PET substrates with Method 4. Flexible memory devices provide the Pτ of ~75 μC/cm² and an absolutely predominant switching speed of 57 ns at 4 V (Fig. 8a). In this bending status with 10 mm radius, more than 50% polarization remained after 10¹⁰ switching cycles and retention time of the devices is expected to be longer than 10 years, as shown in Fig. 8b [50]. Besides, Zhu et al. reported the flexible ferroelectric memory devices on the biocompatible mica substrate. The direct fabrication via van der Waals epitaxy, instead of transferring method, is applied for single-crystalline flexible PbZr0.2Ti0.8O3 growth with SrRuO3 electrode layer (Method 5). This can reduce defect density caused by the lattice mismatch and the clamping effect coming from the weak interaction, between the film and the substrate, which can improve the superior performance of flexible inorganic memory. To be specific, the flexible PbZr0.2Ti0.8O3 ferroelectric memory device keeps its remarkable ability even when it is bent to the radius of 2.5 mm. Robust retention capability of 10⁴ cycles mechanical bending of this device is observed, which attributes to its admirable crystalline quality. The retention time and 10⁶ cycles of polarization switching fatigue test in different status are shown in Fig. 8c [50]. Another class of typical ferroelectric materials applying in ferroelectric memory is the layered perovskite structure Bi1.25La0.75Ti3O12. Flexible and transparent mica with 10 µm thickness is also employed as the substrate here. The flexible Pt/SrRuO3/Bi1.25La0.75Ti3O12/Pt memories have been achieved by pulsed laser deposition. Fatigue tests of 10⁹ switching cycles and 10⁴ times bending cycles with 1.4 mm radius are carried out, almost no fatigue or damage being obtained. It is noteworthy that the red, green and purple laser light illumination effects are also explored at 20–200 °C and the flexible memory device can operate normally [8]. Furthermore, Gao and her coworkers prepared the transparent, flexible, fatigue-free and nonvolatile ferroelectric memory device with the Bi3.23La0.77Ti3O12 ferroelectric film, as shown in Fig. 9a, b [60]. The 1.2 wt % Ag-doped (Ag-ITO) (Ag-ITO) bottom electrode layer is employed to design the transparent mica/Ag-ITO/Bi3.23La0.77Ti3O12/ITO memory. ~80% transmittance for visible lights and 3 mm bending radius are on active service in the memory device, and at the same time, the flexible anti-fatigue property of this memory device makes it stand for 10⁸ switching cycles. This transparent anti-fatigue memory device can use cooperatively with the contact lenses, pictures shown in Fig. 9c, d.

Similarly, (Mn,Ti)-codoped BiFeO3 film is fabricated on flexible mica substrate directly with Pt and Au as the bottom and top electrodes. The bending radius can be as low as 2 mm and the retention time shows as 10⁵ s with fatigue resistance of 10⁹ switching cycles. BiFeO3-based ferroelectric memories also provide the up-and-coming prospective in flexible electronics [74].

Serving in harsh environment is the advantage capacity of ferroelectric memories among the numerous kinds of memory devices. High-temperature stability, resistance to corrosion and high pressure withstanding are investigated widely by researchers [75,76]. The above flexible ferroelectric perovskite oxide memory devices are with comprehensive performance for wearable industrial applications, such as high speed, almost infinite times read-write cycles, as well as harsh environment adaptability. The flexible ferroelectric memory devices are facing the challenge of improving storage density, enhancing the compatibility with semiconductor process by avoiding the contamination of production line, approaching the industrial property value to theoretical level and, moreover, applying the ferroelectric domain wall for information recording to achieve higher information density. Several properties of flexible ferroelectric memory devices, including some organic materials and resistance switching memories, are compared in Table 1, as a summary of the flexible memories.

### 4. Flexible piezoelectric sensors

Sensors are aimed at detecting, converting and bridging the gap between in suit measured physical quantity and the signal of easy-processing energy form, in a variety of environmental conditions, especially in nano-scale, harsh and flexibility required situation. Advancements in sensor manufacturing technologies have raised

---

**Fig. 8.** Properties of flexible memory devices based on the PbZr0.2Ti0.8O3. (a) P-E loops before and after 100 times mechanical compressing, stretching, and releasing cycles of the substrate, and (b) Anti-fatigue test for 3 × 10⁹ switching cycles of PET/SrRuO3/PbZr0.2Ti0.8O3 memory devices. (c) P-E hysteresis loops of mica/ITO/SrRuO3/PbZr0.2Ti0.8O3 flexible ferroelectric memory under various tensile and compressive bending radii, and (d) 10⁹ cycles polarization switching fatigue test in a flat, compressive or tensile bending status for 1000 cycle conditions, respectively. Panel a-b reprinted with permission from ref 50. Copyright 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. Panel c-d reprinted with permission from ref 57. Copyright 2019, Rights Managed by American Association for the Advancement of Science.

**Fig. 9.** Detailed structure and applications of the flexible mica/Ag-ITO/Bi3.23La0.77Ti3O12(BLT)/ITO memory device. (a, b) Structure of memories. (c) Flexible memory using cooperatively with the contact lenses and (d) together on an artificial eye. Reprinted with permission from Ref. 60. Copyright 2018 American Chemical Society.
actuated by micro and miniaturization trend, wearable devices demand, high-speed and low-cost industry applications. The main physical sensors include piezoelectric sensors, piezoresistive sensors, electromagnetic sensors, thermoelectric sensors, photoelectric sensors and optical fiber sensors. Flexible perovskite oxides materials play a vital role here, as the excellent properties and eminent environmental adaptability [77]. They have shown remarkable value in both military and civil fields, such as flexible and portable wearable medical devices [78–80].

Mechanical strain and electric property coupling effect has been occupied the research throne of the hot topic due to the important fundamental theory value and the heavy practical application benefit, especially facing the increasing demand of flexible and wearable Micro-Electro-Mechanical System (MEMS) systems [81–83]. The kinds of mechanical sources that stimulate electrical signal generating [84,85] can be vibration, pressure, stretch [86,87] or even acoustic waves [88,89], succeeding in versatile small-scale flexible sensors in a wealth kinds of operating environment for general and special adhibitions [84,85].

PbZr0.52Ti0.48O3 stands for a supply of ferroelectric materials that are one of the paramount candidates for flexible micro-electro-mechanical sensors. In flexible electronic devices, one should notice that the properties are determined by many factors, including film composition, orientation, bending strain and so on. Plentiful papers have been published to disclose the inner mechanism and keep moving on the enhancement of their serving performance in the meantime [90–92]. For example, Noh et al. developed a flexible touch sensor based on PbZr0.52Ti0.48O3 thin films, according to the proportional relationship between the amount of pressure applied to the piezoelectric materials and the voltage signals generated by the materials, which is shown in Eq. (1).

$$E = \frac{Fd_{33}t}{wl}$$  \hspace{1cm} Eq. (1)

Where $E$ denotes output electric field, $F$ standing for external pressure force, $d_{33}$ indicating the piezoelectric coefficient, $t,w$ and $l$ being the thickness, width and length of the piezoelectric layer. Transfer technology has been employed via laser lift-off method to the PbZr0.52Ti0.48O3 thin films from the rigid sapphire substrate to a flexible polyimide substrate, which is introduced in Method 3. Fig. 10 shows that the touch sensor can clearly draw an obvious distinction between the touch signal and the bending signal by one order difference in output voltage. The single touch duration capability can be identified via the interval between positive and negative peaks and the output signal is above 350 mV.

**Table 1**

<table>
<thead>
<tr>
<th>FE film</th>
<th>sub.</th>
<th>meth.No.</th>
<th>elect.</th>
<th>Ps, Pr (μC/cm²)</th>
<th>speed (ns)</th>
<th>fatig. (N)</th>
<th>temp. (°C)</th>
<th>radius (mm)</th>
<th>cycle (N)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbZr0.2Ti0.8O3</td>
<td>SrTiO3 to PET</td>
<td>4</td>
<td>SrRuO3 Au</td>
<td>90, 75</td>
<td>57</td>
<td>1010</td>
<td>--</td>
<td>10</td>
<td>102</td>
<td>[50]</td>
</tr>
<tr>
<td>PbZr0.52Ti0.48O3</td>
<td>Mica</td>
<td>5</td>
<td>Pt</td>
<td>--, 30</td>
<td>--</td>
<td>109</td>
<td>200</td>
<td>2</td>
<td>103</td>
<td>[69]</td>
</tr>
<tr>
<td>PbZr0.52Ti0.48O3</td>
<td>Si</td>
<td>2</td>
<td>Pt</td>
<td>41, 14</td>
<td>--</td>
<td>109</td>
<td>225</td>
<td>12.5</td>
<td>109</td>
<td>[71]</td>
</tr>
<tr>
<td>PbZr0.35Ti0.65O3</td>
<td>Si to Pt</td>
<td>2</td>
<td>Pt</td>
<td>40, 30</td>
<td>103</td>
<td>9</td>
<td>200</td>
<td>--</td>
<td></td>
<td>[46]</td>
</tr>
<tr>
<td>BiLa0.25Ti1.75O3</td>
<td>Mica</td>
<td>5</td>
<td>Pt</td>
<td>20, 10</td>
<td>&lt;50</td>
<td>109</td>
<td>200</td>
<td>1.4</td>
<td>104</td>
<td>[8]</td>
</tr>
<tr>
<td>BiFe0.93Mn0.07O3</td>
<td>Mica</td>
<td>5</td>
<td>Pt</td>
<td>93, 66</td>
<td>--</td>
<td>109</td>
<td>200</td>
<td>2–4</td>
<td>103</td>
<td>[74]</td>
</tr>
<tr>
<td>BaTi0.95Co0.05O3</td>
<td>Mica</td>
<td>5</td>
<td>Pt</td>
<td>--</td>
<td>105</td>
<td>180</td>
<td>1.4</td>
<td>104</td>
<td></td>
<td>[59]</td>
</tr>
<tr>
<td>P(VDF-TrFE)</td>
<td>PDMS</td>
<td>1</td>
<td>Au</td>
<td>41</td>
<td>140</td>
<td>6</td>
<td>200</td>
<td>--</td>
<td></td>
<td>[34]</td>
</tr>
<tr>
<td>P(VDF-TrFE)</td>
<td>PI</td>
<td>1</td>
<td>Al</td>
<td>--</td>
<td>200</td>
<td>--</td>
<td>10</td>
<td>200</td>
<td></td>
<td>[33]</td>
</tr>
</tbody>
</table>

Fig. 10. The property curves of PbZr0.52Ti0.48O3-based flexible sensor. The signals and their duration of (a) touch motions and (b) bending motions. Reprinted with permission from Ref. [93]. Copyright 2019 Elsevier B.V.
Piezoelectric materials generate electric energy (output voltage) by the form of impulsive signals which can be detected only during the movement in transition between on/off modes. As a result, pressure sensors based on piezoelectric materials are conventionally provided to dynamic pressures measurement. Chen et al. nonetheless, developed a special kind of flexible static pressure sensor with respect to piezoelectric effect of the piezoelectric PbTiO₃ nanowires (PTNWs) combining with the change of carrier scattering of graphene. As observed in Fig. 11a-b, the PTNWs/graphene composites can perfectly seize the static pressure signal by comparing the sensor behavior for each part of this transistor. This remarkable sensor is able to sensitively catch the static pressures up to 9.4 × 10⁻³ kPa⁻¹. Besides, its response time is as low as 5–7 m s, showing tremendous applicable possibility within electronic skin and wearable devices industry.

To get close to medical industry applications, researchers investigated implantable biomedical energy nanogenerators to facilitate the contribution to practical people livelihood [95,96]. Dagdeviren and coworkers reported a sol-gel method fabricated PbZr₀.₅₂Ti₀.₄₈O₃-based flexible skin-mounted sensors for pressure, which is able to be active during daily routines (Fig. 11c-d). The flexible sensing device combing array of square elements ferroelectric and semiconductor manifests the sensitivity of testing pressure as low as 0.005 Pa and response time as fast as 0.1 m s (Fig. 12c). Here, Eq. (2) is provided to explain the dependence of the piezoelectric voltage on contact force.

$$V_p = \alpha AF$$  \hspace{1cm} (2)

Where $V_p$ is the piezoelectric voltage and $\alpha$ denotes the PbZr₀.₅₂Ti₀.₄₈O₃ materials constants as well as each substrate deformation mechanics. $A$ is the contact area between the PbZr₀.₅₂Ti₀.₄₈O₃ element and the weight, and at last, $F$ is the contact pressure [97].

Coincidentally Tseng et al. have reported a lead zirconium titanate-based tactile sensor for body biomedical monitoring. The thin film is fabricated by sol-gel method on the flexible stainless steel substrate [98]. The sensor, with the sensitivity of 0.798 mV/g, is applied to measure several diverse topology areas’ human pulses, including carotid, brachial, finger, ankle, radial artery, and the apical region, respectively. As for acoustic sensors, biomimetic artificial hair cells are mimicked with the new strategy by flexible PET substrate deposited PbZr₁₋ₓTiₓO₃ thin film, where laser lift-off method is utilized. The sensitivity of piezoelectric signals of 45 μV–60 μV is obtained (Fig. 12a) [99]. Furthermore, Thanh D. Nguyen et al. prepared the neuronal cells mechanical deformations sensor with PbZr₁₋ₓTiₓO₃ nanoribbons and cells deflect by 1 nm when 120 mV is applied to the cell membrane (Fig. 12 b-c) [100]. The arrays of PZT nanoribbons can be transferred onto a silicone elastomer and measure mechanical deformations on a cow lung that mimics respiration, thus the PZT nanoribbons offer a minimally invasive and scalable platform for electromechanical biosensing. Besides, electromechanical model coupling the piezoelectric effect with heart motion is developed, so is the vibration control finite element formulation of thin films [90,101], which significantly serve to support and enhance the related performance and biocompatibility with the respect to theoretical aspect.

5. Flexible energy generators based on ferroelectric films

Energy issues hold an increasingly momentous place in global society. Ambient mechanical sources such as solar energy, wind energy, and hydroenergy are in effective utilization as renewable energy resources for energy harvesting. When it comes to micro-electro-mechanical systems, such as wearable electronics or implantable biomedical devices, energy generators of sustainability, self-sufficiency and low-cost power sources are in great request [36,102]. Furthermore, in respect to the raise of energy effective availability, avoiding energy harvesting wasting, energy management is brought to the forefront in the energy research field. As a result, capacitors and cells have drawn considerable attention.

Perovskite piezoelectric materials are outstanding candidates for harvesting or converting mechanical energy, where strain or vibrational energy sources are converted from human activities including stretching motions, pressure, fraction and bending into electrical energy, this time not for detecting the signals as sensors, but to supply the flexible devices under stretchable and flexible condition (Fig. 13) [36,103–105].

In this area of research, considerable research achievements are introduced by Z. Wang, who is also first in line to develop piezoelectric generators of ZnO in 2006 [106], which paved a light way for flexible generators. PZT [48], BaTiO₃ [37,38,107] and other perovskite materials based flexible nanogenerators are studied one after the other by the researchers all over the world, among which innovative approaches of transferring flexible ferroelectric material, such as (1-x) Pb(Mg₁/₃Nb₂/₃)O₃–xPbTiO₃, BaTiO₃, PbZr₁₋ₓTiₓO₃ to flexible substrates have been reported since 2010. Using the crystallized amorphous Pb(Zr,Ti)O₃ thin film transferred by the laser lift-off process from sapphire substrate to a receiver plastic substrate (i.e. Method 3), Park et al. reported a flexible sensor with output voltage of 200 V and current density of 150 μA/cm² by deforming slightly. The light up of a commercial LED arrays via bending motions from human fingers is achieved by this sensor [48]. Taking BaTiO₃ as another example, super-elastic and ultra-flexible BaTiO₃, as an excellent candidate for flexible energy conversion devices as well as memories and sensors, has been reported by Dong and the coworkers. The Sr₃Al₂O₆ sacrificial layer contributes to the −180° foldable freestanding membranes in a damage-free lifting-off process. The super-elasticity mechanism of
Ferroelectric nanodomains dynamic evolution is also discovered [131]. Besides, Park et al. synthesized the thin film by radio frequency magnetron sputtering, which is transferred to a flexible substrate afterwards connecting by interdigitated electrodes for outputting. The BaTiO$_3$ generator can reach up to 1.0 V output voltage and 0.19 $\mu$A/cm$^2$ current density by bending deformation [45].

Directly approaches to fabricate ferroelectric materials on flexible substrates without transferring process are also reported. Won et al. investigated strain-tuned Pb(Zr,Ti)O$_3$ thin films-based flexible vibrational piezoelectric energy harvester, of which the maximum power is 5.6 $\mu$W with the corresponding peak voltage of 690 mV, systematically (Fig. 14a, b). To deliver on the flexibility, austenitic
steel metal foil is selected as the substrate reasonably, where the spin-coating deposited Pb(Zr,Ti)O_{3} polarization of 50 μC/cm^{2} shows an improvement compared with the film on Pt/Si rigid substrates at the same condition [53]. Another state-of-the-art flexible ferroelectric energy harvester of Pb(Zr_{0.52}Ti_{0.48})O_{3} is fabricated by sol spin-coating method directly on the flexible mica substrate. The large scale all-inorganic flexible device exhibits outstanding energy harvesting performance of 120 V open-circuit voltage, 42.7 mW/cm^{2} power density, -0.28 μA short-circuit current and 150 μA/cm^{2} short-circuit current density during periodically bending and unbending processes, given in Fig. 14c, d, e [108].

Despite enjoying above outstanding results of single-component flexible energy generators, the researchers have another modality of flexible energy generators, hybrid ceramic-polymer composite energy generators. Hybrid nanocomposite flexible generator devices advent apparently as an inescapable trend due to their combination of both flexibility and high efficiency, each deriving from the inherence of single materials [39,109,110]. The hydrothermal method is a common process employed in fabricating hybrid composite generators. As shown in Fig. 15a, P(VDF-TrFE) piezoelectric copolymer, in this hybrid composite, serves as the piezoelectric matrix, due to its representative easy polarization and crystallization of polar β-phase. The piezoelectric-hybrid nanocomposite generator of BaTiO_{3} nanowire-employed P(VDF-TrFE) harvested output signal reaching up to ~14 V and ~4 μA, shown in Fig. 15b, which is in a relatively high current level of piezoceramic film-based flexible energy harvesters. Spin-coating method is applied during the fabrication of the polymeric nanocomposite on ITO-coated PET sheet [40]. Additionally, PDMS and graphitic carbons are also selected as the candidates to combine with high level inherent piezoelectric property BaTiO_{3} to get approach to the lead-free stretchable nanogenerators (Fig. 15c, e). The peak open-circuit voltage and short-circuit current are of 5.5 V, 3.2 V and 350 nA, -300 nA in the composite energy generators, respectively (Fig. 15 d). Turning out that the nanocomposites generators have access to operate optoelectronic or organic electronic device applications (Fig. 15f). It is worthy to mention, as most hybrid composite generators preparation, the nanofillers of BaTiO_{3} is embedded in the polymer by hydrothermal synthesis method [36,41]. The part where BaTiO_{3} perovskite oxide material is employed as the flexible energy generators has not ended up. Mixed in PDMS polymer matrix without a toxic dispersion enhancer, the hydrothermally grown BaTiO_{3} nanowires is produced as a flexible piezoelectric nanocomposite energy generator, which is able to light up the liquid crystal displays with 7.0 V output voltage and 360 nA current, respectively [40 Park KI]. Beside Barium oxide family, NaNiO_{3} is also investigated by Jung et al. as a nontoxic, cost-effective, and easily accessible flexible piezoelectric energy generator candidate material. The device synthesized by a NaNbO_{3} nanowire-PDMS polymer exhibits an output voltage of 3.2 V and output current of 72 nA (current density of 16 nA/cm^{2}) when a compressive strain of 0.23% puts on it [41].

Being identical to flexible ferroelectric perovskite oxides in sensor applications, the flexible generators have also been widely studied to be employed in biomedical fields or be making progress towards this goal. Flexible energy harvesters have successfully performed as an alternative to the battery, especially for in vivo implantation (Table 2) [111]. A real-time functional electrical stimulation for beating a live rat’s artificial heart as a self-powered cardiac pacemaker is reported based on 0.72 Pb(Mg_{1/3}Nb_{2/3})O_{3}-0.28PbTiO_{3} single crystal with μm-scale thickness, provided in Fig. 16a-d. The transfer process of the thin film from bulk rigid substrate to a flexible organic one was optimized, thanks to the inherent residual stress of Ni film, forming a stress-controlled exfoliating way (Method 6). Bending and unbending periodic mechanical motions were performed to generate a maximum output

Fig. 15. (a) Schematic illustration of flexible ferroelectric BaTiO_{3} nanowire-embedded P(VDF-TrFE) nanocomposite. (b) The open-circuit voltage in bending and unbending motions. (c) Schematic illustration of BaTiO_{3} nanotubes/PDMS composite, where inset is SEM image of the composite. (d) Generated open-circuit voltage of the as-developed NG under compress stress of 1 MPa. (e) Scheme of the BaTiO_{3} based flexible nanocomposite generator device structure. (f) Photography of operating LED in a darkroom by the flexible nanocomposites energy generator. Panel a-b reprinted with permission from ref 39. Copyright 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. Panel c-d reprinted with permission from ref 37. Copyright 2012 American Chemical Society. Panel e-f reprinted with permission from ref 36. Copyright 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
current and voltage by this flexible energy harvester, reaching up to 145 μA and 8.2 V, respectively, functioning to turn on 50 commercial green LEDs [61]. With the μm-scale-thickness 0.5 mol% Mn in 0.4 Pb(Mg1/3Nb2/3)O3/C0.6PbTiO3 single crystal, the new formed flexible energy harvester is investigated by attaching to the porcine heart, where 17.8 V open-circuit voltage and 1.74 μA short-circuit current are harvested from the porcine heartbeats [62].

Table 2
Comparison of several kinds of flexible ferroelectric perovskite oxides generators, where ferroelectric (FE) film, substrate (sub.), preparation method introduced before (meth.), output voltage (out-V), output current (out-I), output current density (out-J), minimum bending radius (radius), power density (power-D) and reference (Ref) are given.

<table>
<thead>
<tr>
<th>FE film</th>
<th>sub.</th>
<th>meth.</th>
<th>out-V (V)</th>
<th>out-I (μA)</th>
<th>out-J (μA/cm²)</th>
<th>radius (mm)</th>
<th>Power- D (mW/cm³)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbZr0.52Ti0.48O3</td>
<td>sapphire</td>
<td>3</td>
<td>200</td>
<td>1.5</td>
<td>150</td>
<td>16.1</td>
<td>17.5</td>
<td>[48]</td>
</tr>
<tr>
<td>BaTiO3</td>
<td>Si to Kapton</td>
<td>2</td>
<td>1</td>
<td>0.026</td>
<td>0.19</td>
<td>10</td>
<td>7</td>
<td>[45]</td>
</tr>
<tr>
<td>PbZr0.52Ti0.48O3</td>
<td>steel foil</td>
<td>5</td>
<td>0.69</td>
<td>0.06</td>
<td></td>
<td></td>
<td>0.0056 mW</td>
<td>[53]</td>
</tr>
<tr>
<td>PbZr0.52Ti0.48O3</td>
<td>Mica</td>
<td>5</td>
<td>120</td>
<td>0.28</td>
<td>150</td>
<td>2.2</td>
<td>42.7</td>
<td>[109]</td>
</tr>
<tr>
<td>BaTiO3 + (P(VDF-TrFE))</td>
<td>PET</td>
<td>1</td>
<td>14</td>
<td>4</td>
<td></td>
<td></td>
<td>10</td>
<td>0.0015 mW</td>
</tr>
<tr>
<td>BaTiO3 + PDMS</td>
<td>Kapton</td>
<td>1</td>
<td>3.2</td>
<td>-0.30</td>
<td></td>
<td></td>
<td>8</td>
<td>–</td>
</tr>
<tr>
<td>BaTiO3 + PDMS</td>
<td>Polystyrene</td>
<td>1</td>
<td>5.5</td>
<td>0.35</td>
<td>0.35</td>
<td></td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>BaTiO3 + PDMS</td>
<td>PET</td>
<td>1</td>
<td>7</td>
<td>0.36</td>
<td></td>
<td></td>
<td>–</td>
<td>0.0012 mW</td>
</tr>
<tr>
<td>NaNbO3 + PDMS</td>
<td>Kapton polyimide</td>
<td>3</td>
<td>3.2</td>
<td>0.072</td>
<td>0.016</td>
<td></td>
<td>0.6</td>
<td>–</td>
</tr>
<tr>
<td>BaTiO3 + PDMS</td>
<td>polyimide</td>
<td>1</td>
<td>75</td>
<td>15</td>
<td></td>
<td></td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>0.72 Pb(Mg1/3Nb2/3)O3–0.28PbTiO3</td>
<td>Si to PET</td>
<td>6</td>
<td>8.2</td>
<td>145</td>
<td></td>
<td></td>
<td>10</td>
<td>–</td>
</tr>
<tr>
<td>0.4 Pb(Mg1/3Nb2/3)O3–0.6 Pb(Zr,Ti)O3–0.005Mn</td>
<td>Si to PET</td>
<td>2</td>
<td>17.8</td>
<td>1.74</td>
<td></td>
<td></td>
<td>20</td>
<td>–</td>
</tr>
<tr>
<td>Pb(In0.5Nb1.5)O3–Pb(Mg1/3Nb2/3)O3–PbTiO3</td>
<td>PET</td>
<td>1</td>
<td>11</td>
<td>570</td>
<td>100000</td>
<td></td>
<td>20.5</td>
<td>0.7 mW</td>
</tr>
<tr>
<td>Pb(Zr0.52Ti0.48)O3 + PDMS</td>
<td>PI</td>
<td>1</td>
<td>8.3</td>
<td>0.15</td>
<td></td>
<td></td>
<td>25</td>
<td>0.18 μW/cm²</td>
</tr>
<tr>
<td>KNbO3 + PDMS</td>
<td>none</td>
<td>1</td>
<td>2.5 × 10⁻³</td>
<td>2.5 × 10⁻⁵</td>
<td></td>
<td></td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>0.4 Pb(Mg1/3Nb2/3)O3–0.6 Pb(Zr,Ti)O3–0.005Mn</td>
<td>none</td>
<td>1</td>
<td>1.6</td>
<td>10⁻⁴</td>
<td></td>
<td></td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

![Fig. 16](image-url) Fig. 16. (a) An artificial cardiac pace using electrical energy from the flexible PMN-PT energy harvester, (b) flexible PMN-PT sensor stimulating the heart of living rat, (c) recording electrocardiogram of a normal rat heart and (d) the heartbeat arise from the stimuli. (e) Schematic diagrams of a flexible PZT mechanical energy harvester (MEH), and (f) such harvester and its battery mounted on a bovine heart during expansion (Left) and relaxation (Right). Panel a-d reprinted with permission from ref 61. Copyright 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. Panel e-f reprinted with permission from ref 47. Copyright 2014 National Academy of Sciences.
of a mouse is able to give a high output current of 0.57 mA by the flexible energy harvester based on the \( \mu \text{m-scale thickness} \) Pb\((\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3\)-\(\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\)-\(\text{PbTiO}_3\) single crystal \[63\]. Furthermore, an integrated module system based on \(\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3\)-\(\text{PDMS}\) sandwiched between the top and bottom electrodes is established by Dagdeviren et al. to harvest and storage energy from different organs motions \(\text{Fig. 16e}\) \[47\]. Such system enables high efficiency mechanical-to-electrical energy conversion from the natural contractile and relaxation motions of the lung, heart, and diaphragm in several animal models \(\text{Fig. 16f}\). This is one the possible development directions to approach further steps among in vivo biomedical energy harvester based on flexible ferroelectric perovskite oxides.

As one brunch of pyroelectric materials, ferroelectric perovskite oxides are endowed with the instinct for pyroelectric generators \([42,112]\). The flexible nanogenerators can generate electronic signals from temperature-related activity, heated or cooled, in virtue of its pyroelectric characteristics. The flexible pyroelectric generators can, in turn, serve as temperature sensors \[113\].

Starting at this point, the flexible composite pyroelectric generator based on \(\text{KNbO}_3\) nanowires and PDMS polymer is researched \[42\]. Like the common fabricating method talked above in flexible composite piezoelectric generators (Method 1), the simple hydrothermal method is applied here as a rule. The sunlight illumination inductive temperature changes from 295 K to 298 K contribute the 2.5 mV output voltage and 25 pA current peaks, respectively. Moreover, owing to the ferroelectricity of \(\text{KNbO}_3\), the polarization directions can be tuned by electric field from random to unify, which can bring up the nontoxic flexible pyroelectric generator to a large-scale. Breaking through from stiffness ratio, \(\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3\) is composed with PDMS in a novel framework of three-dimensional microfoams instead of low dimensional form \[43\]. The generator being imbued of the flexibility works in principle of both pyroelectricity and piezoelectricity, simultaneously. Temperature fluctuation appearing from 25 °C to 35 °C results in the pyroelectric generating output voltage and current of 1.6 V and 100 pA, respectively, which supported by the finite element results. An inspiring result comes up subsequently, the synchronous mechanical and thermal stimulation applying on the flexible pyroelectric generators giving rise to the superimposed effect of an output voltage of 6.5 V, compared with the 5 V and 1.6 V, separately. Entering the biomedical field, micropatterned single-crystal 0.7 \(\text{Pb}(\text{Mg,Nb})_3\text{O}_3\)-0.3\(\text{PbTiO}_3\) ribbons are explored as a flexible piezoelectric-pyroelectric human-activity energy harvester as well as the sensor \[90\]. When temperature varies from 295 to 303 K (\(\text{dT}/\text{dt} = 0.2 \text{K/s}\)), 0.1 V, 20 nA and 2 mW/cm\(^2\) of output voltage, current peaks and peak power density are observed, respectively. Human hand temperature change test has also been conducted. According to the pyroelectric current \(I\) defining Eq. (3) and \(0.7 \text{Pb}(\text{Mg,Nb})_3\text{O}_3\)-0.3\(\text{PbTiO}_3\) ribbons pyroelectric coefficient is calculated of \(\approx 980 \mu \text{C/cm}^2 \text{K}\).

\[
I = pA(\text{dT}/\text{dt}) \quad \text{Eq. (3)}
\]

Where \(p\) defines the pyroelectric coefficient, \(A\) is the electrode area, and \(\text{dT}/\text{dt}\) notes the temperature change rate. The flexible pyroelectric energy generator can also scavenge mechanical energy from human activities and perceive the sound stimuli, as well as working for photo detecting. More than that, ferroelectric \(\text{BiFeO}_3\) also has the quality to prepare for flexible photodetectors \[114\].

6. Flexible energy storage devices based on ferroelectric films

When energy that is efficiently generated or harvested does not be consumed immediately, energy storage issue comes out as the second part of energy management \[115,116\]. Capacitors rise up as a key master in response to energy management in respect of storage field at the proper time \[117\]. Energy generators and capacitors are never the contradiction of each other. For instance, flexible ferroelectric nanorod \(\text{KNbO}_3\)-PDMS composite presents both high output voltage as a generator and low dielectric loss as a high-k capacitor, the lead-free component, at the same time, preventing any undesirable subsequent pollution or side effects in multipurpose applications \[118\]. Capacitors reports can track back to 1995, when Araujo et al. described the ferroelectric materials among layered perovskite oxides with anti-fatigue property of switching polarization cycles up to \(10^{12}\) \[119\]. With the current rapid development of wearable miniaturized and integrated electronic devices, capacitors with flexibility, high permittivity, low loss and large tunability become a significant research trend.

Gao et al. studied the \(\text{Ba}_{0.67}\text{Sr}_{0.33}\text{TiO}_3\) dielectric thin film based capacitor as a potential flexible microwave electronic application \[120\]. Pt and \(\text{SrRuO}_3\) are top and bottom electrodes of the sandwich structure of \(\text{mica}/\text{SrRuO}_3/\text{Ba}_{0.67}\text{Sr}_{0.33}\text{TiO}_3/\text{Pt}\) \(\text{Fig. 17a}\), where the capacitor device is synthesized on the flexible mica substrate by PLD system. The device demonstrates a large dielectric constant over 1200, a low loss tangent of 0.16 and low frequencies tunability of 67%, which appears no obvious degradation in bending radius of 5 mm \(\text{Fig. 17b}\), even endured 12000 bending cycles. Microwave dielectric properties are measured simultaneously where \(\text{Fig. 17c}\) depicts the test device schematic of shielded resonant cavity method. \(\text{Fig. 17d}\) illustrates the dielectric constant and loss tangent of the flexible ferroelectric capacitor at 18.6 GHz, a decrease by 80 emerging among dielectric constant and the stable value remains for loss tangent undergoing 20000 bending cycles.

Another all-inorganic flexible dielectric film based capacitors have been obtained by Liang et al. currently \[121\]. The desirable performance of \(\text{Pt}/\text{Ba}_{0.67}\text{Sr}_{0.33}\text{TiO}_3/\text{ITO}/\text{mica}\) capacitor is expressed in energy density of 40.6 J/cm\(^3\) and energy efficiency of 68.9%, which declares no declination undergoing 4 mm radius bending cycles for \(10^4\) times, respectively. As a versatile flexible energy storage device, it can be on the action service at a wide temperature
range from −120 °C to 150 °C maintaining the energy density over 15 J/cm³ and energy efficiency more than 70%. The structure diagram and the discharging property are shown in Fig. 18. The energy density of 34.6 J/cm³ is liberated by BaZr0.35Ti0.65O3 capacitor, drawing an ultrahigh power density of \( PD = 3.2 \text{ MW/cm}^3 \), at 4.23 MV/cm, from t0 to t0.9 which presents the required time for discharging 90% of the loaded energy. Both the fast charge/discharge rates (t0.9 = 10.7 s) and high power density of this flexible ferroelectric capacitor are satisfying for the applications in energy storage devices, for instance, the power inverter and DRAM [121].

Furthermore, antiferroelectric ferroelectric perovskite oxides, such as PbZrO3 and Pb0.94La0.06Zr0.97Ti0.03O3, are fabricated by sol-gel/spin-coating method for assembling the flexible energy storage capacitors on metal foil substrates [122,123]. To enhance the electrical property, Pb0.94La0.06Zr0.97O3 is applied as the dielectric layer. At the same time, to have a better understanding of energy density of the flexible ferroelectric capacitors, we state Eq. (4) related to polarization as follows:

\[
U_{\text{tot}} = \int_{0}^{P_{\text{max}}} |EdP| \quad \text{Eq. (4)}
\]

Where \( U_{\text{tot}} \) stands for the energy density and \( E \) is the applied electric field. \( P \) is the ferroelectric polarization [124–126].

Comparative with the 15.8 J/cm³ energy-storage density of Pb0.94La0.06Zr0.97Ti0.03O3 based flexible capacitor, Pb0.94La0.04ZrO3 based capacitor provides the energy density of 15.2 J/cm³ with the energy loss of ~4.8 J/cm³. Both flexible capacitors show high fatigue properties when bends to 2.5 mm bending radius for more than 1000 bending cycles with no noticeable degradation in energy storage parameters, among which the maximum value of the discharge and discharge time could be adjusted by the bending radius of Pb0.94La0.04Zr0.97Ti0.03O3 film.

It is well-known, BaTiO3 multilayer energy storage capacitor is famous for its high energy storage density, low dielectric loss, high breakdown strength [127]. For example, sandwiching flexible poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) layer by two flexible BaTiO3-P(VDF-HFP) neighboring layers, the flexible capacitor shows the breakdown strength of 315 kV/mm and energy storage density of 5.22 J/cm³, several-fold higher than those of single-layer one [128]. Different from neighbor layers structure, P(VDF-HFP) is employed as a polymer matrix composited with BaTiO3@TiO2 core-shell particles. Spin-coating method is used for deposition. The flexible small-scale multilayer capacitor possesses discharged energy density as high as 2.5 J/cm³ at its breakdown field of 166 MV/m and its stored energy of nine-layer capacitor reach up to 0.54 J [129]. Different from both methods mentioned above, a blended architecture of PVDF-BaTiO3-PVDF flexible multilayer nanocomposite film is built by spin-coating layer by layer, with heating plates. The BaTiO3-rich layer and PVDF-rich layer work together to obtain the maximum breakdown strength of 495 kV/mm and discharged energy density of 19.37 J/cm³, attributes to the reduced electric concentration due to the structure of BaTiO3 large interfacial area [130].

Fascinating performances are observed in these flexible capacitors, which endow them with enormous potential in the future energy storage application system for flexible electronics, such as modern wearable devices and electrical power systems.

7. Conclusion and perspectives

It is firmly believed that ferroelectric perovskite materials have a bright future in flexible electronic devices, according to their high performance and the research achievements which scholars have gained. This review presents systematic discussion of these flexible ferroelectric perovskite oxides based nano-scale electronic devices in regards to emphasizing partially on three fundamental emergent parts: flexible ferroelectric memories, flexible piezoelectric sensors and flexible energy generators. At this stage, high speed, large polarization and fatigue-free flexible memories have been reported; high-sensitive and nano-scale flexible sensors are investigated; high output single and small-bending-radius nano-generators are researched. Splendent grades though the researchers achieved in ferroelectric perovskite oxides flexible electronic devices, the perfect level they are not in, which puts it in the situation where more effects and deeper steps are required.

Theory and practice are the guides to each other. The scholars are always trying to keep the theoretical knowledge and practical devices development mutually, neck and neck, but some bumpy terrain gets in the way. Speaking to the theoretical mechanism, there is a promotion space in the coupling effect research of mechanics, electricity and optics related to these flexible devices. The understanding of mechanism and relationship of these parameters is a challenge, as it may become more complicated when it comes to nano-scale or low-dimensional order of magnitudes. Things probably have a way of getting promoted this breakthrough with the professional assistance of theoretical calculation and analogue simulation, proposing the patterns from various viewpoints.

Comparing to organic flexible electronic devices, the relative stable perovskite oxides-based devices possess predominance of high performance, such as higher polarization, lower operation voltage and higher piezoelectric coefficients, but facing the relatively high-cost, superfluous steps for flexibility, at the same time. To achieve improvements in this area, we can pay attention to (1) the discovery of optimized material system selection. Choosing from the bulk system regarding more of the properties or from the direct low-dimensional thin film system with a different viewpoint regarding more of the flexibility and properties as well. Doping, technically is a good way to improve them, additionally. (2) Proceeding with the large-scale and low-cost ferroelectric material fabrication. Materials structure or even domain structure value in flexible devices properties, so does the material geometrical configuration. On the basis of uniformity in materials with no defects, the designs of device shape determine its stretch ability, to a great extent.

With great efforts dedicated on the materials selection, approach, fabrication method and properties attention, researchers have been made some improvements in the harsh environment as well as biomedical industries, which focus on implantable flexible nano-scale sensors and energy generators. There is still a long way to go before proof-of-concept ferroelectrics based flexible in vivo...
electronics are commercially available, though. Compatibility of most ferroelectric materials and a living body is one of the issues, which requests non-toxic ferroelectric candidates selection and the proper methods in synthesis process, guaranteeing no hidden trouble in service. Furthermore, developing other kinds of flexible ferroelectric perovskite-oxide based devices depending on their different properties, such as pyroelectric and triboelectric properties, is another direction to explore. In that case, expanding the range of application areas with multi-functional signals simultaneously in one flexible improved properties electronic device is concluded.

Enhancing the performance of existing ferroelectric perovskites for flexible devices is no doubt a long road to go. To broaden the path, adding new members, for example, by synthesizing new composites, to the flexible ferroelectric perovskites oxides family for flexible nano-scale device applications is perhaps a shortcut. Behind this path, countless optimistic perovskite oxide material scholars are speeding up the process for academic research and society demands, both, with endless exploration as well as trial and error. The endlessly admirable achievements of flexible ferroelectric based devices in condensed matters are not far away.

Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

Acknowledgements

The work is supported by the National Natural Science Foundation of China (51790492, 51431006, 51902159 and 61874055) and the National Key Research Program of China (2016YFA0300101).

References


[128] WenXiu Gao received her Ph.D. degree in School of Ma- terials Science and Engineering, Nanjing University of Sci- ence and Technology in 2009 before joining Prof. Guoliang Yuan’s research group as a research assistant. During her Ph.D. period, she was jointly educated in Temple University in America from Nov. 2016 to Nov. 2017 and worked as a visiting scholar in UC Berkeley R. Ramesh’s group for several months right after Ph.D. graduation. Her research interest is mainly focused on the flexible ferroelectric materials and related devices.

[129] Yi Zhu is a master student of Materials Science of School of Materials Science and Engineering, Nanjing University of Science & Technology, China, under the supervision of Prof. Guoliang Yuan. His research focuses on the flexible inor- ganic ferroelectric films and their applications on FeRAM.

[130] Guoliang Yuan is currently a professor in the School of Materials Science and Engineering, Nanjing University of Science and Technology, China. He received his Ph.D. de- gree from Nanjing University in 2004. Then he joined Department of Applied Physics, The Hong Kong Poly- technic University and worked as an Alexander von Humboldt research fellow in Bonn University from 2006 to 2007 and JSPS research fellow in Tsukuba University from 2008 to 2009. He joined Nanjing University of Science and Technology in 2009. His research focuses on ferroelectric, piezoelectric, and multiferroic thin films and devices.

[131] Jun-Ming Liu is a Professor of Physics with Department of Physics and Laboratory of Solid-State Microstructures, Nanjing University. He obtained his Ph.D. degree from Northwestern Polytechnical University in 1989 before joining the Department of Physics, Nanjing University. He specializes in correlated quantum materials and computa- tional materials sciences. He has co-authored more than 600 technical papers in international refereed journals. More information can be found at http://pld.nju.edu.cn. Email: liuqm@nju.edu.cn.