Piezoelectric thin films: an integrated review of transducers and energy harvesting

To cite this article: Asif Khan et al 2016 Smart Mater. Struct. 25 053002

View the article online for updates and enhancements.

Related content
- A review of piezoelectric polymers as functional materials for electromechanical transducers
  Khaled S Ramadan, D Sameoto and S Evoy
- Topical Review
  S Tadigadapa and K Mateti
- Review of piezoelectric micromachined ultrasonic transducers and their applications
  Joontaek Jung, Wonjun Lee, Woojin Kang et al.

Recent citations
- Strain-tuning of the optical properties of semiconductor nanomaterials by integration onto piezoelectric actuators
  Javier Martin-Sánchez et al.
- Computational model for power optimization of piezoelectric vibration energy harvesters with material homogenization
  A.M. Matos et al.
- Effect of thermo-magneto-electro-mechanical fields on the bending behaviors of a three-layered nanoplate based on sinusoidal shear-deformation plate theory
  Mohammed Arefi and Ashraf M Zenkour
Topical Review

Piezoelectric thin films: an integrated review of transducers and energy harvesting

Asif Khan, Zafar Abas, Heung Soo Kim and Il-Kwon Oh

1 Department of Mechanical, Robotics and Energy Engineering, Dongguk University-Seoul, 26 Pil-dong 3-ga, Jung-gu, Seoul 100-715, Korea
2 Department of Mechanical Engineering, School of Mechanical and Aerospace Engineering, Korea Advanced Institute of Science and Technology, 335 Gwahak-ro, Yuseong-gu, Daejeon 305-701, Korea

E-mail: heungsoo@dgu.edu

Received 6 May 2015, revised 14 October 2015
Accepted for publication 3 November 2015
Published 7 April 2016

Abstract
Piezoelectric thin films offer a number of advantages in various applications, such as high energy density harvesters, a wide dynamic range, and high sensitivity sensors, as well as large displacement and low power consumption actuators. This review covers the available material forms and applications of piezoelectric thin films: lead zirconate titanate (PZT)-based thin films, lead-free piezoelectric thin films, piezopolymer films, cellulose-based electroactive paper (EAPap), and many other thin films used for electromechanical transduction. The electromechanical properties and performances of piezoelectric films are compared and their suitability for particular applications are reported. The key ideas of piezoelectric thin films are reviewed and discussed for sensory and actuation systems, energy harvesting, and medical and acoustic transducers. In the last section, an insight into the future outlook and possibilities for thin film-based devices and their integration into real-world applications is presented.

Keywords: thin films, piezoelectrics, sensors, actuators, energy harvesting

(Some figures may appear in colour only in the online journal)

1. Introduction
Piezoelectric materials play key roles in various devices and applications in modern society, ranging from flashing lights to ultrasonic imaging. With their intrinsic electromechanical transduction, applied strain produces an electrical signal, whereas electrical input induces mechanical deformation. Piezoelectric transducers are components of choice in strain sensors, self-powered wireless sensors, acoustic and ultrasonic devices, precision positioning in scanning probe microscopes, fuel injection systems, active damping control, and adaptive control systems.

In the last two decades, there has been a surge in the growth of new piezoelectric crystals, piezopolymers and lead-free piezoelectric materials, resulting in major improvements in electromechanical coefficients, material properties, and application areas [1–3]. This progress in bulk piezoelectrics has been integrated swiftly into thin films due to enhanced growth methods. Piezoelectric thin films assist in developing nanoscale and microscale devices due to the added functionality provided by the electromechanical coupling and their ability to be micromachined. An ever-increasing breadth of piezoelectric thin films as functional materials is evident from their incorporation into micromechanical systems (MEMS) and nanoelectromechanical systems (NEMS) [4, 5].

Piezoelectric thin films are indispensable in understanding highly integrated piezoelectric devices. Two primary crystal structures of thin films are wurtzite and perovskite structures [6, 7]. Nonferroelectric piezoelectrics, such as ZnO and AlN, have wurtzite crystal structures and are suitable for resonator applications at high frequencies. The low piezoelectric coupling coefficients associated with nonferroelectric piezoelectric thin film reduces their appropriateness for displacement actuators. Ferroelectric-piezoelectric thin films
permit the low voltage operation of actuators and high-sensitivity sensors due to the relatively higher piezoelectric coefficient. In perovskite ferroelectrics, several mechanisms contribute to the piezoelectric constants, including polarization extension, polarization rotation, and domain wall motion [8]. Due to their flexible nature and biodegradability, piezopolymer film (PVDF) and cellulose-based piezoelectric electroactive papers have been incorporated into sensing, actuation, energy-harvesting, and medical applications [9–15].

The key attributes of piezoelectrics, including high-frequency resonant structures, low-power sensors with broad dynamic ranges, and large-amplitude actuation with lower driving voltage and hysteresis, along with CMOS compatibility, offer many advantages. In the midst of these advantages, the integration of thin films in piezoelectric devices has become realistic. One significant shortcoming of PZT thin films is the high percentage of lead, by weight, which can be hazardous to the environment due to its toxic nature. However, presently there is no single composition of lead-free piezoelectric material with properties that are as good as those of PZT [16]. Together with bulk piezoelectrics, piezoelectric thin film material devices are gaining more and more importance in innovative applications with the focus on miniaturization and high performance. Lead zirconate titanate thin films are gaining further importance in the area of sensors and actuators due to their excellent piezoelectric properties. These thin films have been used in various novel applications: microaccelerometers [17, 18], ultrasonic and force sensors [19–24], microactuators [25–29], microphones, and energy harvesting transducers [30]. Thin-film PZT-based actuators are the basis for a MEMS inkjet. The integration of ferroelectric thin films with CMOS technology assisted in the development of novel thin-film capacitors. PZT-based thin films are expected to dominate the market of piezoelectric devices, but AlN, ZnO, and other lead-free piezo films will be part of future innovative devices [31, 32]. Piezoelectric polymer thin films are gaining a lot of attention in relation to the development of novel devices due to their excellent material properties and electromechanical behavior. Cellulose EAPap is a recent addition to the piezoelectric family and investigations have been performed to explore its potential in microrobots, flying objects, actuators, and its applications in acoustics [14, 33].

From a literature review, PZT remains the customary material for thin-film devices, but AlN can be valuable in sensing applications due to lower dielectric losses, which translate into a better signal-to-noise ratio and voltage output. PZT is more suitable when current output is used in applications where force, torque and power are important. ZnO has potential in the fabrication of nanoscale self-powered devices. PVDF polymer can be incorporated into many sensor applications. Cellulose electroactive paper is another good candidate for electromechanical transduction applications in green electronic devices requiring biodegradable and biocompatible functions. For electromechanical conversion, a comparison of the figures of merit of different piezoelectric thin films is presented in Table 1.

Table 1. Figures of merit of piezoelectric thin films [61, 92].

<table>
<thead>
<tr>
<th>Material</th>
<th>FOM</th>
<th>PZT</th>
<th>AlN</th>
<th>ZnO</th>
<th>BiFeO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>ε₃₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300–1300</td>
<td>10.5</td>
<td>10.9</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ε₃₁,₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6–18</td>
<td>11.9</td>
<td>10.3</td>
<td>20.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2. PZT thin films

PZT thin films are attractive for use in devices where high piezoelectric coefficients are a primary concern. PZT-based ferroelectric films are the most widely used thin films for piezoelectric transduction. The inherent high piezoelectric coefficient comes at some cost in terms of the intricacy of composition. Thus, it is necessary to develop films that retain stoichiometry, orientation, and phase. Thin films lag behind bulk piezoelectrics in material growth; we have targeted the state of the art applications of thin films in devices at the micro and nano scales. Enhancing piezoelectric coefficients is a major concern in reducing the driving voltage or enhancing the sensitivity of devices. For applications where higher values of piezoelectric coefficients are essential, PZT-based thin films are particularly attractive. Figure 1(a) reports a comparison chart of piezoelectric e₃₁,₄ coefficients over the last few decades.

Deposition of PZT thin films on substrates before fabrication is an efficient method to develop sensing and actuating functionalities in microdevices. Devices or arrays of devices that combine electronics with other components, such as sensors, transducers, and actuators, are often fabricated as integrated circuits where the substrate or the element deposited on the substrate is micromachined. PZT-based thin film microsensors and actuators offer many advantages in terms of a high blocking force, good actuating range, low power consumption, and a relatively wide frequency range of operation, compared with competitor technologies [19, 20]. The integration of piezoelectric PZT thin film deposited by chemical solution deposition (CSD) on silicon-based cantilevers for micromirror and microrelay applications has been investigated, as shown in figure 1(b) [27]. For 390 μm long cantilever structures, tip deflections of up to 20 μm at an applied voltage of 10 V were measured. The piezoelectric coefficient d₃₁ was measured to be −12 pCN⁻¹. Levy et al reported single-crystal lead zinc niobate-lead titanate films in monomorph actuators [34]. Freestanding films were fabricated by slicing a 7 μm-thick layer off the crystal bulk and assembling it into a flexural actuator, thus circumventing polycrystalline deposition techniques. Deflections of 1 μm were observed at 100 V for 1 mm long films. A comprehensive study was carried out to measure the piezoelectric properties of PZT thin films on a metallic substrate prepared by a sol-gel process. The values of d₃₃ were about 29 pCN⁻¹ and have been compared with former measurements of the piezomodulus d₃₃ [35, 36]. Piezoelectric-driven microcantilevers using PZT thin films have been characterized for nanostorage or atomic force microscopy (AFM) [37]. The micro-cantilever had a resonant frequency of 17.3 kHz and
the corresponding displacement of 2.36 μm at an applied bias of 1 V. The piezoelectric coefficient \(d_{31}\) of the PZT cantilever was \(-56.4 \text{ pmV}^{-1}\).

Fabrication and characterization results of piezoelectric acoustic sensors and micromachined ultrasonic transducers (pMUTs) based on 2 μm-thick (PZT) thin films were promising [24, 38]. The resonances show relatively large Q factors, which can be partially explained by the small diameters as compared with the sound wavelength in air and in the test liquid (Fluorinert 77). A transmit–receive experiment with two quasi-identical pMUTs was performed showing significant signal transmission up to a distance of 20 cm in air and 2 cm in the test liquid. The work from the Muralt group was considered as a basis for the application of an ultrasonic transducer in medical imaging and materials testing. A model of a tri-axial micro accelerometer that consists of a quadri-beam suspension, a seismic mass, and displacement transducers using piezoelectric thin films was studied [39, 40]. The electrodes are configured and interconnected to measure one out-of-plane acceleration and two in-plane accelerations. A micromachined piezoelectric force sensor [20] was considered a breakthrough in the design of scanning force microscopy (SFM) as well as a good example of an integrated piezoelectric microdevice. PZT thin films inherit piezoelectric coefficients enabling the development of micro- sensors and actuators and future self-power generators.

Energy scavenging from ambient vibration and other motion sources has attracted much interest, particularly as a micropower source for wireless sensors. The working duty cycle of most wireless sensor nodes can be quite small, so that mW supply levels enable some autonomy. This implies that supplying a power of less than 100 μW is adequate to operate wireless nodes in silent mode. Piezoelectric thin films are frequently characterized for MEMS energy harvesting devices and their effective transverse and longitudinal piezoelectric coefficients have been investigated [41, 42]. The transformation from mechanical to electrical energy is done using a piezoelectric material microgenerator. In a microgenerator, piezoelectric film is excited by an external vibration source at resonance. Vibrations from machinery usually have a frequency of \(\sim 100\) Hz, which is rather low for microsystems, given that resonant frequencies increase with decreasing size and mass. The inclusion of a soft elastic body can be helpful in attaining a resonant frequency of around 100 Hz. MEMS piezoelectric energy-harvesting devices can power a wireless sensor used for structural health monitoring without replacing batteries. Thin-film lead zirconate titanate, \(\text{Pb}(\text{Zr},\text{Ti})\text{O}_3\) (PZT), in a MEMS power-generating device was designed to resonate at specific frequencies from an external vibrational energy source, thereby creating electrical energy via the piezoelectric effect [43]. The corresponding energy density was measured as 0.74 mW h cm\(^{-2}\), which compares favorably to the values for lithium ion batteries. A theoretical prediction of microgenerator power density 310 μW cm\(^{-3}\) at 150 Hz and 2.5 g acceleration can be used as a base for the fabricating energy-harvesting devices [44]. A model for the accurate prediction of the electrical parameters of

![Figure 1](image1.png)

Figure 1. (a) Evolution in piezoelectric \(c_{31, f}\) coefficients [4] (reproduced with permission; copyright 2012 Cambridge University Press). (b) Cross-sectional view of microactuator [27] (reproduced with permission; copyright 2002 Elsevier).

![Figure 2](image2.png)

Figure 2. Typical construction of piezoelectric thin-film energy harvesting MEMS [140] (reproduced with permission; copyright 2012 IOP Publishing).
MEMS-based piezoelectric energy-harvesting devices was presented to compare with experimental results [45]. A typical thin film piezoelectric energy harvesting setup is shown in figure 2. Interdigitated electrode (IDE) systems with a lead zirconate titanate (PZT) thin film configuration generate higher voltages than parallel plate capacitor-type electrode (PPE) structures. Because ceramics tend to crack at relatively moderate tensile stresses, this means that IDEs have a lower risk of cracking than PPEs. For these reasons, IDE systems are ideal for actuators and energy harvesting from vibration [46]. The figure of merit for IDE structures with a larger electrode gap was derived to be twice as large as for PPE structures, for PZT-5H properties. PZT-based ferroelectric thin films are expected to produce high output energy due to high piezoelectric coefficients. However, for certain lead-free thin films, such as AlN, the output energy is very much equivalent to PZT thin films, possibly due to the low dielectric constant of AlN thin films.

3. Lead-free piezoelectric thin films

Most research work has focused on PZT-based thin films for smart applications. However, most commercially available piezoelectric material PZT contains more than 60 weight percent of lead (Pb). Due to the toxic nature of Pb, there is a need to develop lead-free, environment friendly materials as a substitute for PZT with equivalent characteristics to that of PZT-based piezoelectric thin films. Considering all the possible choices, zinc oxide (ZnO), aluminum nitride (AlN), sodium potassium niobate (KNN), bismuth ferrite (BFO), and barium titanate, BaTiO3 (BT), as alternatives to PZT, success has been very limited. In this section, different lead-free piezoelectric thin films employed in various sensors and actuators, and their potential applications in energy harvesting, are presented.

3.1. Aluminum nitride (AlN)

AlN thin films have shown piezoelectric effects that are as good as those of bulk materials. These functional layers are good enough for piezoelectric actuators and sensors [31]. Different techniques have been suggested to increase the piezoelectric response from AlN [32, 47]. The possibility of AlN films deposited by RF sputtering as an actuating element for MEMS applications was investigated [48]. The implementation of ultra thin (100 nm) AlN piezoelectric layers for
the fabrication of vertically deflecting nanoactuators have also shown good results, as shown in figure 3(a) [49]. Vertical deflections as large as 40 nm were observed from 18 μm long and 350 nm thick multilayer cantilever bimorph beams with 2 V actuation. These results make AlN films ideal candidates for the realization of nanoelectromechanical switches for low power logic applications, atomic force microscopy, nanoresonator-based sensing, and energy harvesting. The potential of AlN film to create piezoelectric resonant devices was tested [50]. A micromachined resonator for mass-sensing applications, which is based on a silicon cantilever excited with a sputter-deposited piezoelectric AlN thin film actuator was also reported [51]. The measurements from the cantilevers of the two arrays revealed a quality factor of 155–298 and a mass sensitivity of 120.34 ng Hz$^{-1}$ for the first array, and a quality factor of 130–137 and a mass sensitivity of 104.38 ng Hz$^{-1}$ for the second array. By substituting lead zirconate titanate thin films by AlN on SUS by an electron cyclotron resonance sputtering system showed that piezoelectric coefficients of AlN were very much comparable to PZT thin films [52].

Properties of AlN thin films depend on the deposition technique and deposition conditions. A relatively higher dielectric constant was reported for AlN thin films deposited on p-type Si (100) wafer under ultraviolet (UV) radiation. Sequential injection of trimethylaluminum (TMA) and ammonia was used at a growth temperature of 370 °C [53]. Structural and optical properties of AlN thin film deposited on silicon (100) substrate by pulsed dc (asymmetric bipolar) reactive magnetron sputtering, were evaluated by x-ray
diffraction (GIXRD), atomic force microscope (AFM), spectroscopic ellipsometry, and secondary ion mass spectroscopy (SIMS) [54]. The microstructure, chemistry and optical transmission properties of AlN thin films prepared by unbalanced magnetron sputtering, were reported [55]. The smooth surface of the thin film with an average roughness of 6.464 nm makes it suitable for application in surface acoustic wave devices.

Figure 5. (a) PET substrate with lump structures prototype, (b) Al/PET substrate, (c) power generator prototype and (d) SEM diagrams of ZnO film at 75 W [72] (reproduced with permission; copyright 2010 Elsevier).

Figure 6. Room temperature values of $d_{33}$ as a function of TC for various piezoceramics [76] (reproduced with permission; copyright 2007 Springer).

Figure 7. Output power as a function of load resistance: (a) KNN/Si and (b) PZT/Si [85] (reproduced with permission; copyright 2012 Elsevier).
3.2. Zinc oxide (ZnO)

Zinc oxide piezoelectric thin film is a key material in miniaturizing electronic devices and has been used in MEMS and NEMS systems as an actuator, sensor, surface acoustic wave (SAW) filter, bulk acoustic wave (BAW) resonator and for harvesting energy from the environment [57–60]. AlN and ZnO thin films exhibit similar piezoelectric properties; the transverse coefficient is almost equal, while the longitudinal effect is somewhat larger in ZnO. ZnO is more frequently studied in MEMS applications than AlN due to the better availability of ZnO thin films and less demanding vacuum conditions [61]. The performance of a PZT/ZnO actuator in response to reducing gas atmospheres was tested [62, 63]. It was found that the applied voltage is distributed to both plates in air, but concentrates in the PZT part in a reducing-gas atmosphere due to a decrease in resistance of the ZnO part. A high-aspect-ratio (HAR) nanotip integrated microcantilever ZnO piezoelectric actuator [64], with an HAR nanotip of 6 μm side length, over 18 μm height, and which was built on the 85 μm wide, 300 μm long, and 1.2 μm thick cantilever, was studied. The aspect ratio of the tip was three or more and the tip radius was less than 15 nm. The simulated spring constant and the resonance frequency were 1.4 N m⁻¹ and 27.81 kHz, respectively.

One of the most promising applications of ZnO thin film is a differential liquid flow sensor [65], as presented in figure 4(a). The fabricated liquid flow sensor has been tested with a piezoelectric micropump for flow rates from 30 to 300 μL h⁻¹. Properties of the diamond cantilever AFM probes of various dimensions and of 5 μm in thickness with a 1 μm thick ZnO sensor and actuator were calculated [66]. The resolution of displacement and actuation force for a probe of 150 μm in length and 50 μm in width were estimated to be about 1.5 nm. A novel flow sensing and vibration sensing application of ZnO thin films was studied [67, 68]. ZnO thin film annealed at 300 °C showed relatively better results in vibration sensing studies. It generated a comparatively higher peak output voltage of 147 mV, due to improved structural and morphological properties, and a higher piezoelectric $d_{31}$ coefficient value (figure 4(b)).

A literature review reveals that the properties of ZnO films depend on the deposition methods and conditions. The electrical, structural and optical properties of ZnO thin films deposited by the spatial atomic layer deposition (ALD) technique, have been analyzed [69]. Spatial ALD was shown to be a possible means for the deposition of highly conductive and transparent ZnO at a high growth rate of up to ~1 nm s⁻¹. Using a pulsed laser deposition technique at low temperature, low resistivity and highly transparent Al-, B- and Ga-doped ZnO conducting films for thin film solar cell applications, were fabricated [70]. For ZnO:Al, a minimum resistivity was found to be $2.5 \times 10^{-4} \Omega \cdot \text{cm}$ with mobility and carrier concentrations of $44 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ and $5.7 \times 10^{20} \text{cm}^{-3}$, respectively. Using the ultrasonic spray technique, indium doped ZnO thin films were deposited on glass substrate [71]. Electrical resistivity of $3.42 \times 10^{-3} \Omega \cdot \text{cm}$ and optical transmittance, in the visible range, of 50%–70% was reported.

**Figure 8.** Illustration of the KNN-based energy harvester [86] (reproduced with permission; copyright 2013 IOP Publishing).

**Figure 9.** (a) Micrograph and (b) schematic structure of the fabricated vibrational energy harvester using the BiFeO$_3$ film and the measurement setup [92] (reproduced with permission; copyright 2013 The Japan Society of Applied Physics).
ZnO thin film in piezoelectric energy harvesting represents a new and potentially important branch of nanotechnology. The aim of the characterization of ZnO thin film is to embed materials, such as textiles with nanosized generators that convert otherwise wasted mechanical energy into electricity. Another possibility is to allow nanoelectromechanical (NEMS) systems to be self-powered, analogous to the aim of piezoelectric energy harvesting for larger scale systems. A new design of the PET-based (polyethylene terephthalate) flexible power harvesting system, consisting of flexible PET vibration substrate, piezoelectric ZnO thin film, lump structures, and electrodes has been proposed [72]. The generator achieves a maximum open-circuit voltage (OCV) of up to 2.25 V and a closed-circuit voltage (CCV) of up to 1.55 V, as shown in figure 5. Integrating a high-performance ZnO piezoelectric transducer with a flexible stainless steel substrate (SUS304) to construct a wind-power generator was reported [58]. A mass loading of 0.57 g at the front end of the cantilever was critical to increasing the amplitude of vibration and the power generated by the piezoelectric transducer. After rectification and filtering through a 3.3 nF capacitor, the output power of the wind generators exhibited a specific power output of 1.0 μW cm⁻² with a load resistance of 5 MΩ. More recently, a ZnO nanostructure array has been characterized for harvesting solar energy [73], ecofriendly biomechanical energy [74], and an ultra flexible nanogenerator for harvesting energy from respiration [75].

3.3. Potassium sodium niobate (KNN)

KNN piezoelectric thin films have been widely investigated in recent times as an alternative to PZT-based piezoelectric materials. KNN dielectric properties and electromechanical coupling constants are very much comparable to those of PZT thin films, which can enable the development of environment friendly microsensors, microactuators, and piezoelectric energy generators [76]. A comparison of piezoelectric coefficients is shown in figure 6. Conventionally, devices with KNN thin films are microfabricated by wet- or dry-etching techniques [77] or photolithography. Higher values of transverse piezoelectric coefficient can be obtained by depositing the films by RF magnetron sputtering [78]. The properties of KNN microfabricated functional layers have been studied for energy storage [79–81], and characterized at the nanoscale [82]. Significantly enhanced piezoelectric properties originated from the nanodomains were confirmed by transmission electron microscopy [83].

Recently, piezoelectric thin films have been used frequently in medical devices and for diagnoses inside the human body. KNN, due to its nontoxic nature, is a good candidate for implantable cardiomechanical electric sensor (CMES) applications [84]. The performance of PZT thin films was compared with KNN for vibration energy harvesting: 1.1 μW and 1.0 μW power outputs were measured for PZT/Si and KNN/Si unimorph cantilevers (figures 7(a), (b)) [85]. A micromachined energy harvester, a 2 μm thick KNN film, was deposited on a silicon cantilever integrated with a proof mass, as shown in figure 8 [86]. The energy harvester achieved an output power of 731 nW and a normalized power density (NPD) of 2.29 μW g⁻² mm⁻³ at the resonant frequency of 1509 Hz with the acceleration of 10 ms⁻². Piezoelectric MEMS energy harvesters (EHs) of lead-free KNN thin films on microfabricated stainless steel cantilevers were also investigated [87], 2.2 μm thick KNN thin films were directly deposited by RF magnetron sputtering onto the cantilevers; an average output power of 1.6 μW at 393 Hz and 10 ms⁻² from the lead-free unimorph cantilever was obtained.

3.4. Other materials

Many other lead-free ferroelectric thin films, such as barium titanate BaTiO₃ (BT), bismuth sodium titanate (BNT), Ba (Ti₀.₉₅Zr₀.₀₅)O₃ (BTZ), bismuth ferrite BiFeO₃ (BFO), and sodium bismuth titanate (NB), have been characterized to obtain reasonable piezoelectric coupling coefficients. For the BTZ thin film (x = 0.20) fabricated using an alkoxide solution with partial hydrolysis, the grain and crystallite size were increased, and the dielectric constant and d₃₃ were improved, to 253 and 8.9 mm V⁻¹ respectively [88]. BNT-based thin films are potential candidates for lead-free piezoelectrics, and
frequency similar to 98 Hz produced an output voltage of 1.5 V g$^{-1}$ and an electrical power of 2.8 μW mm$^{-1}$ g$^{-2}$ (g = 9.8 m s$^{-2}$) at a load resistance of 1 MΩ. The generalized electromechanical coupling factor was estimated to be 0.41% and results were comparable to those of the best-performing vibrational energy harvesters using other piezoelectric films. A schematic structure of the fabricated vibrational energy harvester using the BiFeO$_3$ film is shown in figure 9.

4. Piezopolymer thin films

Piezopolymers such as polyvinylidene fluoride (PVDF) films have been widely investigated as a sensor and transducer material due to their chemical stability and high piezoelectric, pyroelectric, and ferroelectric properties. The piezoelectric properties of PVDF films can be activated by mechanical treatment, stretching, or poling. PVDF’s ability to couple mechanical and electrical properties, intrinsic biocompatibility, lightness of weight, and reasonable mechanical strength unwrap many areas of research including medical, biological, optical, and aerospace. PVDF film has high flexibility, compared with ceramics and single-crystal piezoelectric materials. PVDF actuators have been used for speaker applications [93]. The development of wearable electronics makes it possible to monitor abnormalities in the human body [94], and a novel device for monitoring cardiorespiratory signals is presented in figure 10 [95]. PVDF films have been employed as a sensory receptor of skin to test its validity as a tactile sensor for fingerprint measurements [96].

Health monitoring and diagnosis is critical for large flexible structures in order to protect the structure during operation. Structural health monitoring methods using the changes in resonant frequencies based on an array of PVDF films can diagnose both the damage and its severity [97]. Removable sensors are essential in applications like health monitoring or the nondestructive evaluation of newly produced or finished composite structures. In such tests, a major requirement is that the tested structures are not altered during either bonding or the removal of the sensor. The characterization of a PVDF film sensor was effective as an acoustic emission sensor used in structural health monitoring online [98]. PVDF film sensors have been reported to have been used for the detection of defects such as impact damage and delaminations in structures [9].

A triangular-shaped PVDF film has also been characterized as a position sensor [99]. The resonance frequencies match well with commercial sensors and good coherence over a wide frequency range was observed. PVDF film is a proven material in many sensing applications including, but not limited to, material identification sensors [100], pressure sensors [101], adaptive vibration control [102], and for investigating the dynamic response of vibrating structures [103, 104]. Simultaneous sensing and actuation are desirable in microrobotic and biomedical applications. A sensor-actuator, ionic polymer-metal composite actuators using PVDF film for performing and monitoring open-loop microinjection of living Drosophila embryos, was studied [10].
Replacing metallic electrodes by conducting polymer poly (ethylene dioxythiophene) (PEDOT-PSS) on poly(vinylidene fluoride) enhances the response in both sensor and actuator applications [105]. A novel electro-active polymer actuator based on a blended polymer membrane of sulfonated poly (ether ether ketone) (SPEEK) and PVDF for a cost-effective and high-performance polymer actuator with controllable stiffness has also been studied [106].

The value of PVDF thin film piezoelectric coefficients are sufficient to generate an acceptable voltage under strain. A number of devices for piezoelectric energy harvesting from PVDF thin film have been investigated [107–109]. The design of a novel PVDF piezoelectric backpack generated a moderate output power, 45.6 mW, to power portable electronics [110]. The amount of electrical energy obtained from a copolymer polyethylene–polypropylene PE–PP foil with a thickness of 11 μm for a single step of a duration of 1 s from walking energy was 340 nJ [111]. A study of a piezoelectric energy harvester for parasite mechanical energy in shoes shows that it provides an average output power of 1 mW at a frequency of 1 Hz during human walking, which demonstrates the possibility of applying a piezoelectric energy transducer to power wearable sensors [108]. Piezoelectric polyvinylidene fluoride (PVDF) microbelts have been reported to convert the energy from low-speed air flow to electricity via their resonant oscillation. The micrometer-thick PVDF thin films were fabricated by a top-down reactive ion etching process, and were able to generate sufficient electrical energy from low speed air flow for the sustained operation of small electronic devices, as demonstrated in figure 11 [112].

5. Piezoelectric electro-active paper

The surge in cellulose research has prompted the development of novel, ecofriendly, and biocompatible materials. The discovery of piezoelectricity in wood was reported very early on, in 1950. Nevertheless, the potential of cellulose as a smart material was only reported in the last decade [113]. This smart cellulose was named electro-active paper (EAPap). EAPap was fabricated by depositing metal electrodes on both sides of a cellulose film. The actuation mechanism of EAPap is a combination of the piezoelectric effect and ion migration, associated with the dipole moment of the cellulose paper ingredients. A concept figure for cellulose EAPap actuation is shown in figure 12. Cellulose is a naturally occurring electro-active polymer and exhibits smart characteristics, such as being ultra lightweight, ease of manufacturing, large strain in response to an electric field, good mechanical properties, and ease of processing. These promising characteristics support the exploitation of cellulose as a smart material for vibration and strain sensors for structural health monitoring [114, 115], bending and hybrid actuators [12, 116–119], micro electromechanical devices, and a possible flexible energy-harvesting transducer for self-powered sensors [15, 120]. A study of future possibilities and challenges in cellulose-based EAPap research showed that cellulose EAPap has a lot of potential for use in various applications [33]. Due to a smart actuation mechanism, cellulose EAPap can be used in applications such as micro insect robots, micro flying objects, flexible electrical displays, and biosensors.

It is important to investigate the mechanical properties and electromechanical behavior of cellulose EAPap under different environmental conditions in order for it to realize its...
Mechanical properties vary under different humidity and temperature conditions. The initial Young’s modulus of EAPap was in the range of 4–9 GPa, which was higher than that of other polymer materials. Also, the Young’s modulus is orientation-dependent, which may be associated with the piezoelectricity of EAPap materials (figure 13(a)). The elastic strength and stiffness decrease gradually when the humidity and temperature are increased. EAPap is a complex anisotropic material and creeps at elevated temperature, but there is insignificant creep at room temperature. The elastic behavior varies inversely with temperature and with the bias angle; the viscous behavior of EAPap is relatively complex [123]. A study of the hygrothermal behaviour of cellulose EAPap and its microscale

Figure 13. (a) Typical pull test result of cellulose EAPap [121] (reproduced with permission; copyright 2008 IOP Publishing). (b) Speaker performance measurement setup in an anechoic chamber [14] (reproduced with permission; copyright 2011 Springer).
characterization showed that creep strain depends on relative humidity and temperature, and the EAPap structure changes due to creep deformation [124, 125].

The direct piezoelectric effect of EAPap was quantified by a quasistatic relation between induced charge and applied stress. The measured piezoelectric charge constant was in the range of 8–28.2 pC N⁻¹, which is similar to that of piezopolymers (PVDF) [126]. A bending actuation model of chitosan-blended cellulose (CBC) EAPap can be useful in investigating the electromechanical actuation behavior of EAPap devices such as artificial muscles, microrobots, and various other actuators [127, 128]. The study of polarization behavior and dielectric properties reveals that EAPap behavior is similar to that of electret polymers [129]. Higher piezoelectric coefficients for transduction applications are vital. The wet drawing method with different conditioning and electrically aligned regenerated cellulose films are effective in enhancing the mechanical stiffness and piezoelectricity of EAPap [130–132].

The electro-active paper actuation voltage per unit thickness is very low compared with other EAP materials. When 0.25 kV mm⁻¹ of excitation voltage was applied to the paper actuator, 4.3 mm of tip displacement was observed with a 40 mm long paper sample [133]. A custom built force transducer was used to measure the blocked force of EAPap; the measurements were accurately down to micronewton resolution under both ac and dc excitation [134]. The inherited actuation mechanism facilitates the advantages of ionic EAP and electronic EAP to be optimized. Thus, EAPap can be used as an artificial muscle [135], and its low excitation voltage is suitable for many other applications, including as an active sound absorbing material, flexible speakers [136], and as a vibration control and vibration sensor element [114, 136]. A schematic diagram of an EAPap flexible speaker is presented in figure 13(b).

More recently, an EAPap actuator for haptic applications [137], and an actuator remotely controlled and powered by microwaves has been presented [138]. Cellulose and one-dimensional nanomaterial composite, cellulose/silica and silica–gold hybrid biomaterials, prepared by sol-gel covalent cross-linking processes, have been tested for various industrial applications due to their enhanced optical, electrical, and mechanical properties [139].

6. Future outlook and possibilities

This review emphasizes the current development and applications of PZT-based thin films, lead-free piezoelectric thin films, piezo-polymer PVDF thin films, and cellulose-based electro-active paper (EAPap). A comprehensive survey of the enhanced piezoelectric response, advances in integration, applications as piezoelectric sensors, actuators, resonators, energy harvesters, and other novel devices, has been presented. Progress in thin-film growth takes advantage of the distinctive characteristics of thin-film piezoelectrics. Future challenges include the development of higher response thin-film piezoelectrics, refined control of surface roughness, and the exploration of nanoscale and microscale piezoelectric devices. When the performances of piezoelectric materials improve, and the integration of diverse devices becomes manufacturable, the contribution of piezoelectric thin-film research becomes essential in continuing the technological progress in both biological and physical sciences. The lead-free piezoelectric thin films will allow the fabrication of products that are ecofriendly and safe.

Piezoelectric thin films have allowed the development of new sensing and actuation devices capable of large displacements at complementary metal oxide semiconductor-compatible voltage levels. It is possible to achieve superior and tailored piezoelectric properties with improved compositions on flexible substrate. Over the last few decades, there have been many improvements in optimizing deposition conditions for thin films on substrates to enhance electromechanical transduction. Control over the growth of the piezoelectric thin films and lead-free compositions of thin films can lead to good environmental stability and responses, coupled with higher piezoelectric coupling coefficients. The progress in high piezoelectric responses in films makes a wide variety of applications possible, including low-voltage radio frequency MEMS switches and resonators, film-type speakers, flying objects, flexible displays, soft haptic devices, actuators for millimeter-scale robotics, droplet ejectors, medical imaging transducers, and energy harvesters for wireless sensors and structural health monitoring.

Acknowledgments

This research was supported by the Basic Science Research Program, through the National Research Foundation of Korea (NRF), funded by the Ministry of Education (2014R1A1A2A10054019).

References

[1] Matsuo K, Xie R J, Akimune Y and Sugiyama T 2002 Preparation of lead-free Sr₂₋ₓÇa(x)Na₆+x⁻Na₀五百xOₓ (x = 0.1)-based piezoceramics with tungsten bronze structure J. Ceram. Soc. Jpn. 110 491–4
[23] Varadan V K and Varadan V V 2000 Microsensors, microelectromechanical systems (MEMS), and electronics for smart structures and systems Smart Mater. Struct. 9 953–72
[34] Levy M, Ghimire S, Bandypadhyay A K, Hong Y K, Moon K, Bakhru S and Bakhru H 2002 Pzt-pt single-crystal thin film monomorph actuator Ferroelectr. Lett. Sect. 29 29–40
properties and residual stress of sputtered AIN thin films for mems applications Sensors Actuators A 115 501–7


[62] Isogai Y, Miyayama Y and Yanagida H 1995 Mechanical response to reducing gases in PZT/ZnO actuator Nippon Seram Kyo Gak. 103 96–8

[63] Isogai Y, Miyayama Y and Yanagida H 1996 PZT/ZnO actuator responding to reducing gases Sensors Actuators B 30 47–53


[73] Jia Z N, Zhang X D, Liu Y, Ma J, Liu C C and Zhao Y 2012 Conductive white back reflector and scatter based on ZnO nanostructure arrays for harvesting solar energy Nano Energy 1 783–8


[75] Lin H I, Wuu D S, Shen K C and Horng R H 2013 Fabrication of an ultra-flexible ZnO nanogenerator for harvesting energy from respiration ECS J. Solid State Technol. 2 P400–4


[90] Kwak J, Kingon A I and Kim S H 2012 Lead-free (Na0.8K0.2)NbO3 thin films for the implantable piezoelectric medical sensor applications Mater. Lett. 82 130–2


Bar H N, Bhat M R and Murthy C R L 2005 Parametric


Lee Y S 2005 A new position sensor using a triangularly shaped piezoelectric pvdf film Advances in Fracture and Strength Pts 1- 4 297–300 2115–21


Shirinov A V and Schomburg W K 2008 Pressure sensor from a PVDF film Sensors Actuators A 142 48–55


Zhao J and You Z 2014 A shoe-embedded piezoelectric energy harvester for wearable sensors Sensors 14 12497–510


Sun C L, Shi J, Bayerl D J and Wang X D 2011 PVDF microbells for harvesting energy from respiration Energ. Environ. Sci. 4 4508–12

Kim J, Yun S and Ounaeiz Z 2006 Discovery of cellulose as a smart material Macromolecules 39 4202–6


Morita T, Kurosawa M and Higuchi T 1995 An ultrasensitive micromotor using a bending cylindrical transducer based on PZT thin film Sensors Actuators A 50 75–80


Kim H S, Kim J, Jung W, Ampolo J, Craft W and Sankar J 2008 Mechanical properties of cellulose electro-active paper under different environmental conditions Smart Mater. Struct. 17 15029


