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General Introduction: Smart Materials, Sensors, and Actuators

The early twenty-first century has foreseen acceleration of innovations in robotics and automations as well as artificial intelligence (AI), where sensors/transducers and smart materials play very important roles. The concept of AI has been around since the late 1950s; however, it's only since the first decade of the twenty-first century that excitement about it has really begun to grow due to the ability of fast computation and abundant size of memory devices. A very successful demonstration of AI is Google's AlphaGo, which is the first computer program to defeat a professional human Go player (see Figure 1.1). Another successful application of AI is the unmanned vehicles and aircrafts where large number of sensors and actuators are used.

One may ask, what is the relation between the key word "ferroic materials" of this book and the mentioned robotics, automations, and AI? The answer is that these smart and intelligence systems rely on large amount of data from sensors and memories for machine learning and actuators for close-looped feedback control systems; and among these sensors, actuators, and memories, ferroic materials play very important roles.

For example, the piezoelectric property of a ferroelectric material (one of the most typical ferroic materials) can be used for ultrasound sensors to detect distance of your car from a wall for auto parking system. A ferroelectric material can be used as the functional element for many kinds of sensors from pressure sensor to acceleration sensor, infrared sensor, etc. Beyond that, a ferroelectric polarization and its switching can also be used in memory devices such as ferroelectric random-access memory (FeRAM) where the ferroelectric layer acts as gate insulator in a field-effect transistor (FET) structure. Ferroelectric tunneling-based resistive random-access memory (RRAM) has also been demonstrated, and such ferroelectric-based memory has been shown to be able to perform as an artificial synapse. More interestingly, artificial neural networks (ANNs) based on these ferroic synapses can realize brain-like computing and AI functions such as image recognition. As shown in Figure 1.2, synapses with $BiFeO_3$ (BFO) ferroelectric layer has been successfully demonstrated.

This book will tell you fundamentals and characterization methods of ferroic materials, physics, and technologies behind ferroic device design and applications as well as their recent advances.

Ferroic Materials for Smart Systems: From Fundamentals to Device Applications,
First Edition. Jiyan Dai.

Figure 1.1 AI beats human chess player.

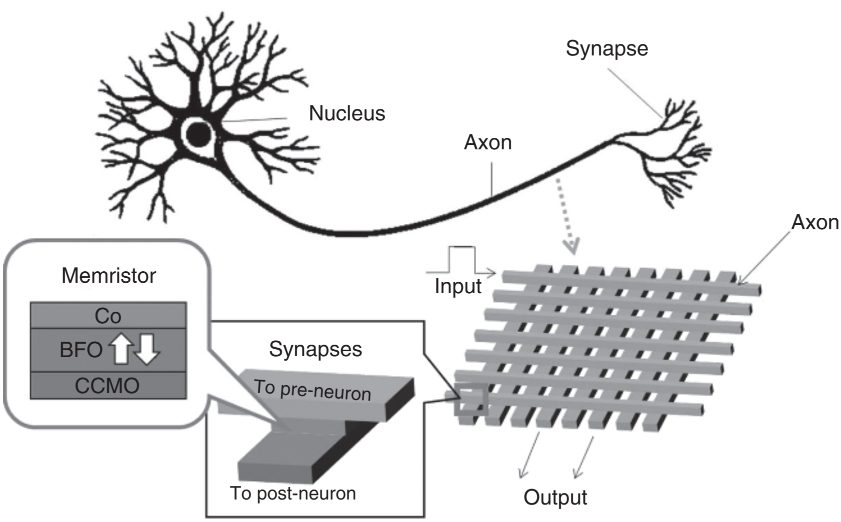


Figure 1.2 A cross-bar structure of synapse and artificial neuron networks based on a cross-bar structure. Ferroelectric thin films such as $BiFeO_3$ can be used as the junction material. Source: Adapted from Boyn et al. (2017).

1.1 Smart System

A smart system, such as a self-driving car or remote-control aircraft, is a system that relies on sensors and actuators to realize instant feedback of controlled variables (CVs) such as speed, height, etc. The basic component of a smart system usually contains sensors, actuators, and control system. An intelligent smart system needs large amount of data processing and memories, while ferromagnetic and ferroelectric materials have been implemented in realizing non-volatile memristors. Beyond that, memories based on ferroelectric thin films may also find application in electronic synapses as building blocks toward building ANN.

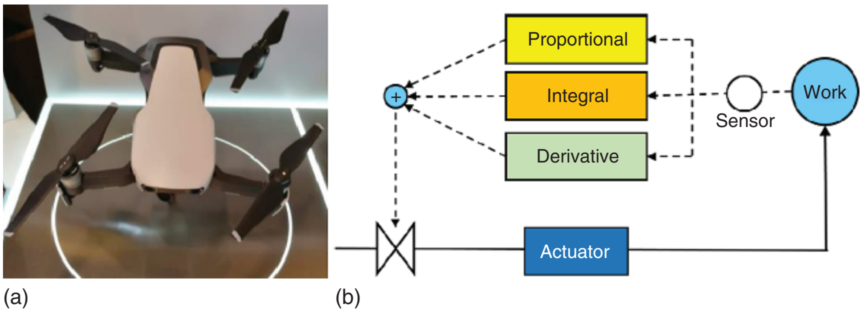


Figure 1.3 (a) Photo of a remote control copter and (b) diagram of a PID feedback control system where sensors and actuators are implemented.

As an example, a smart system of remote control copter relying on proportional–integral–derivative (PID) feedback control system is shown in Figure 1.3. PID is a three-order feedback control system that has been widely used in auto driving vehicles and auto-pilot airplanes to make the dynamic system operate smoothly or being stable during video imaging. Equation (1.1) illustrates the mechanism of PID control where three terms of proportional gain (P), integral gain (I), and derivative feedback (D) can provide instant response to cure the error (E) between the set point (speed of vehicle or height of the copter) and controlled variable (CV):

$$MV(t) = \boldsymbol{P}E(t) + \boldsymbol{I}\int_0^t E(t')dt' - \boldsymbol{D}\frac{dCV(t)}{dt} \tag{1.1}$$

In this feedback control system, we can find applications of ferroic materials, for example, piezoelectric-based gyroscope, surface acoustic wave device for wireless communication, and ferroelectric-based infrared detector. In gyroscope, rotation and acceleration can be sensed by measuring induced voltage generated by piezoelectric effect; a surface acoustic wave device based on piezoelectric effect is used for communication band selection; and a ferroelectric-based infrared detector can be used as an intruder sensor making the copter able to find people for rescue mission. Figure 1.4 shows the finite element modeling (FEM) simulation of three resonant motions in a $Pb(Zr_{x,}Ti_{1-x})O_3$ (PZT)-based gyroscope and photo of a fabricated gyroscope (Chang and Chen 2017).

Sensors: Devices that can "sense" a change in some physical characteristics and perform an electrical input function are commonly called *sensors*. For example, a strain sensor converts mechanical strain into electrical signal.

Actuators: Devices that perform an output function are generally called *actuators*. An actuator can be utilized to control some external moduli or output mechanical movement such as ultrasonic wave. For example, an atomic force microscope (AFM) uses piezoelectric actuators to realize scanning along three directions.

Transducers: Both sensors and actuators are collectively known as *transducers* because they are used to convert energy of one kind into energy of another kind. Transducers can be used to sense a wide range of different energy forms

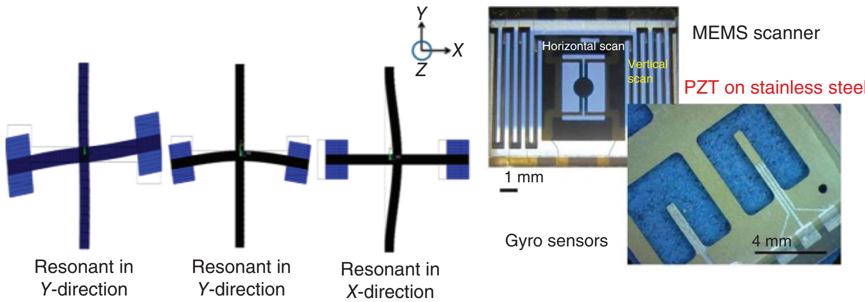


Figure 1.4 FEM simulations of three resonant motions in a PZT-based gyroscope and photo of a fabricated gyroscope. Source: Adapted from Chang and Chen (2017).

such as movement, electrical signals, thermal or magnetic energy, etc. The type of input or output transducers being used really depends on the type of signal or process being "sensed" or "controlled," but we can define a transducer as a device that converts one physical quantity into another.

A smart system needs sensors and actuators to realize the sensing functions such as distance, movement, and acceleration as well as actions. These sensors and actuators use smart materials to realize the conversion between different energies and moduli to electrical signals such as voltage, current, and capacitance. Of course, many sensor devices are made of semiconductors such as the FET, but this is not the focus of this book.

"***Smart material***" is a very large concept, in fact, there is no stupid material (a joke), i.e. all materials are smart in some way since they all have their own properties and response to external stimuli. But in this book, we restrict the "smart materials" to those materials with "ferroic" characteristics. We focus on basic physics, materials science, structures, devices, and applications of ferroic materials for smart systems. The ferroic materials are usually classified as possessing one of the followings based on coupling of stimuli:

(i) ***Ferroelectric***, which is also piezoelectric when electromechanically coupled and pyroelectric when thermoelectrically coupled.
(ii) ***Ferromagnetic***, which is also magnetostrictive when magnetomechanically coupled.
(iii) ***Ferroelastic***, which also includes shape memory when thermomechanically coupled.

Among these ferroics, we can see that strain, electric polarization and magnetization, and their interplay or coupling are involved. We call a material as ferroic material if it possesses at least one of the properties of ferroelectric, ferromagnetic and ferroelastic.

If we look at the diagram shown in Figure 1.5, we can see that the coupling and interplay between electricity, mechanics, magnetism, heat, and optics result in many smart functions, such as ferroelectric, piezoelectric, pyroelectric, ferromagnetic, electromechanical, etc. One book cannot cover all of them, but those belong to ferroic materials and devices especially in the form of thin films will be

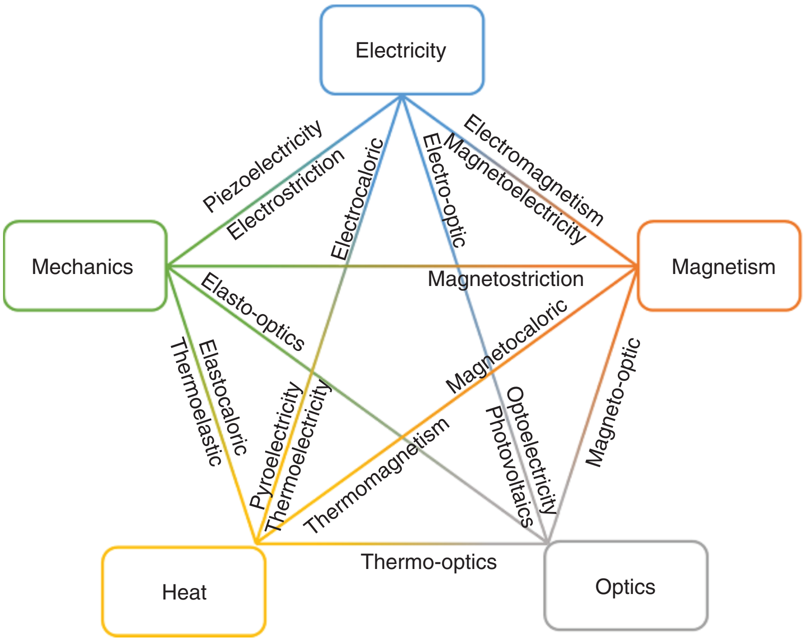


Figure 1.5 Diagram showing coupling between different moduli and the clarification of smart materials.

extensively introduced in this book. Before going into details, some application examples of ferroic materials in smart systems are given in this chapter.

1.2 Device Application of Ferroelectric Materials

When people talk about applications of ferroelectric materials, the first thing jumps out is most possibly the PZT (lead–zirconium–titanate with chemical formula $Pb(Zr_x Ti_{1-x})O_3$), which is known as an excellent piezoelectric material. As the most popular ferroelectric, PZT is also the most important piezoelectric material in commercial applications. Piezoelectric materials have very broad applications in many fields, from medical ultrasound imaging to ultrasonic wire bonding machine in semiconductor industry, from pressure sensors to accelerometer, etc. The market size of piezoelectric materials is more than US $1 billion now and is expected to be US $1.68 billion by 2025 (GRAND VIEW RESEARCH).

Another field of application of ferroelectric materials is the infrared sensors based on their pyroelectric property, which is also one of the most important properties of a ferroelectric material. Beyond these well-known applications, another important application based on the switching of ferroelectric polarization is the non-volatile memory device such as FeRAM. Examples are given in the following and details will be introduced in the following chapters.

1.2.1 Piezoelectric Device Applications

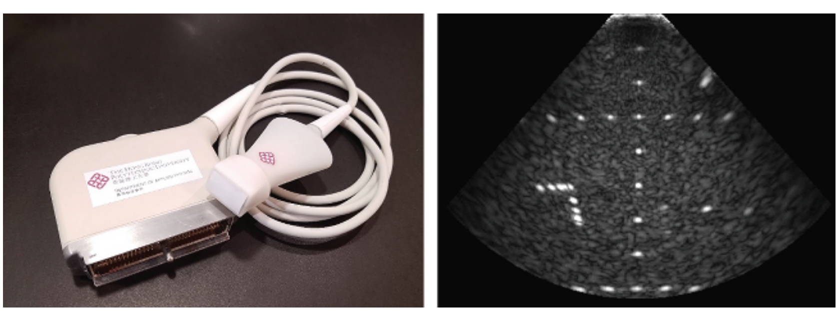
An example of smart system using piezoelectric material is the distance radar system in a car or a sonar system in submarines as shown in Figure 1.6, where the key sensing element is based on piezoelectric material to realize the conversion between electrical energy and acoustic energy for sending and receiving sound waves. Other application examples of piezoelectric devices include active damping system, micro-scanning system in scanning probe imaging instrument (such as AFM), force sensor, accelerometer, energy harvesting, etc.

Medical ultrasound imaging system with piezoelectric material as the transducer to convert electrical and acoustic energies is another very good example of device application where the piezoelectric material plays the roles of sensing and actuating functions. Figure 1.7 shows photos of ultrasound transducers developed in our group. Knowledge in ultrasound transducer fabrication, characterization, and applications will be intensively introduced in Chapter 6.

A very new application example is piezoelectric-based fingerprint ID system in mobile phone. The currently used finger identification system is based on capacitance measurement to obtain two-dimensional (2D) information of fingerprint, but it faces the problem of difficulty to identify the fingerprint when the finger is dirty or wet. Ultrasound fingerprint identification system based on piezoelectric ultrasonic transducer and imaging system can obtain a three-dimensional image

(a) (b)

Figure 1.6 Piezoelectric materials-based sonar system for car (a) and submarine (b).



(a) (b)

Figure 1.7 (a) Transducers and (b) B-mode image of a wire phantom acquired with PolyU-made array ultrasound transducer.

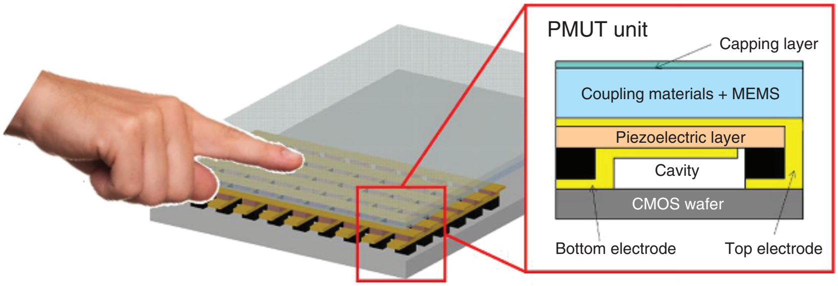


Figure 1.8 Illustration of concept of a ultrasonic transducer-based fingerprint ID system based on complementary metal-oxide-semiconductor micro-electro-mechanical systems (CMOS-MEMS) technology.

of fingerprint with a certain depth. This can overcome the problems of the current fingerprint identification system in most mobile phones. InvenSense, Inc. is one of the main suppliers of this solution, and Figure 1.8 is an illustration of the ultrasonic fingerprint system.

1.2.2 Infrared Sensor

An infrared sensor is usually made of a ferroelectric material, which is also pyroelectric that generates surface electric charges when exposed to heat in the form of infrared radiation. A pyroelectric-based infrared sensor can detect the temperature change but produce no response for a steady temperature since the pyroelectric sensing element can only produce polarization change-induced electric charge when the sensor is subject to temperature change. Figure 1.9a shows a photo of a real infrared detector with its internal device structure illustrated in Figure 1.9b, where the active element is made of pyroelectric materials such as $LiTaO_3$. Those pyroelectric materials with their polarization able to be switched are ferroelectrics. Therefore, pyroelectric sensors that are widely used as infrared detectors are important device applications for ferroic materials in a smart system.

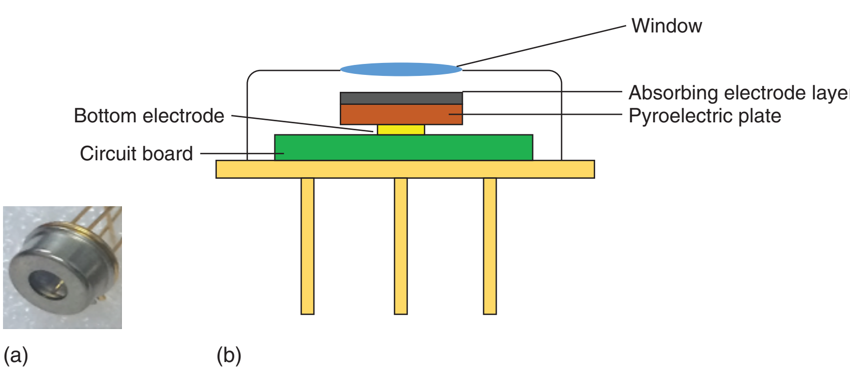


Figure 1.9 A photo of an infrared detector (a) and illustration of its internal structure (b).

1.2.3 Ferroelectric RAM (FeRAM)

Ferroelectric RAM (FeRAM, F-RAM, or FRAM) is a random-access memory that is similar to Dynamic Random Access Memory (DRAM) in structure but uses a ferroelectric layer instead of a dielectric layer to achieve non-volatility. FeRAM is one of a growing member of alternative non-volatile random-access memory technologies that offers the same functionality as flash memory.

Advantages of FeRAM over flash memory include lower power usage, faster write performance, and much greater maximum read/write endurance (about 10^{10}–10^{14} cycles). FeRAMs have data retention of more than 10 years at +85 °C (up to many decades at lower temperatures). Market disadvantages of FeRAM are much lower storage densities than flash devices and higher cost.

A ferroelectric material has a nonlinear relationship between the applied electric field and the stored charge. Specifically, the ferroelectric characteristic has the form of a hysteresis loop, which is very similar in shape to the hysteresis loop of ferromagnetic materials. The dielectric constant of a ferroelectric is typically much higher than that of a linear dielectric because of the effects of electric dipoles formed in the crystal structure of the ferroelectric material. When an external electric field is applied across a dielectric, the dipoles tend to align themselves with the field direction. This alignment process is produced by small shifts in the positions of ions and shifts in the distributions of electric charges in the crystal structure. After the charges are removed, the dipoles retain their polarization state. Binary "0"s and "1"s are stored as one of the two possible electric polarizations in each data storage cell. For example, in Figure 1.10, a "1" is encoded using the negative remnant polarization "$-P_r$," and a "0" is encoded using the positive remnant polarization "$+P_r$". In this FET structure with a ferroelectric layer as gate dielectric, the two polarization states correspond to different V_{th}, resulting in a memory window within which the ON and OFF states of the FET can be read.

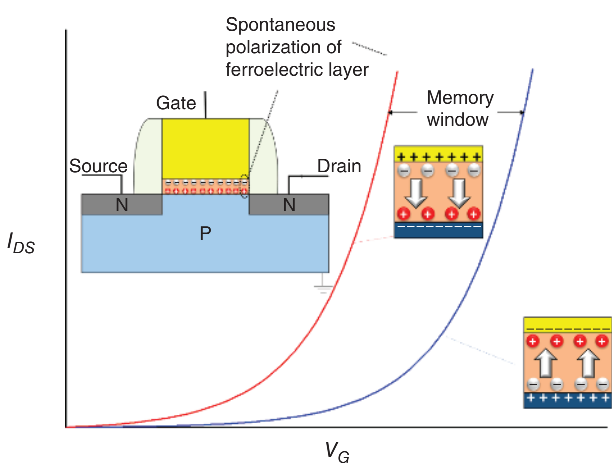


Figure 1.10 Schematic diagram of field-effect transistor (FET) and the current–voltage (*I*–*V*) characteristics induced by two different polarization state.

FeRAM remains a relatively small part of the overall semiconductor market. In 2016, worldwide semiconductor sales were US $338.93 billion (according to WSTS, SIA), with the flash memory market accounting for US $59.2 billion (according to IC insights (Cho 2018)). The 2017 annual revenue growth of Cypress semiconductor, perhaps the major FeRAM vendor, were reported to be US $2.33 billion. The much larger sales of flash memory compared with the alternative FeRAMs support a much larger research and development effort. Flash memory is produced using semiconductor linewidths of 15 nm at Renesas Electronics Corporation (2017). Flash memory can store multiple bits per cell (currently Samsung has announced the 64-layer 512-Gb in the NAND flash devices). As a result of innovations in flash cell design, the number of bits per flash cell is projected to increase to double or even to triple. As a consequence, the areal bit densities of flash memory are much higher than those of FeRAM, and thus the cost per bit of flash memory is orders of magnitude lower than that of FeRAM.

1.3 Device Application of Ferromagnetic Materials

Among many successful applications of ferromagnetic-based devices, memory device based on ferromagnetic material is one of the most successful examples, especially in the thin film form. This is manifested by the very large market of magnetic hard disc in computing systems. But in most recent years, solid state memory (mainly flash memory) is superseding the magnetic hard disc. Nevertheless, ferromagnetic material also finds its application in non-volatile memories such as spin-transfer torque memory.

1.3.1 Spin-Transfer Torque Memory

Spin-transfer torque can be used to flip the active elements in magnetic random-access memory. Spin-transfer torque magnetic random-access memory (STT-RAM or STT-MRAM) has the advantages of lower power consumption and better scalability over conventional magnetoresistive random-access memory (MRAM), which uses magnetic field to flip the active elements. Spin-transfer torque technology has the potential to make possible MRAM devices combining low current requirements and reduced cost; however, the amount of current needed to reorient the magnetization at present is too high for most commercial applications, and the reduction of this current density alone is the basis for present academic research in spin electronics. Figure 1.11 is a schematic diagram of spin valve structure, while arrows indicate the magnetization direction.

1.3.2 Magnetic Field Sensor Based on Multiferroic Device

If a material possesses more than one of the ferroic properties of ferroelectric, ferromagnetic and ferroelastic, it is called multiferroics. Unfortunately, such

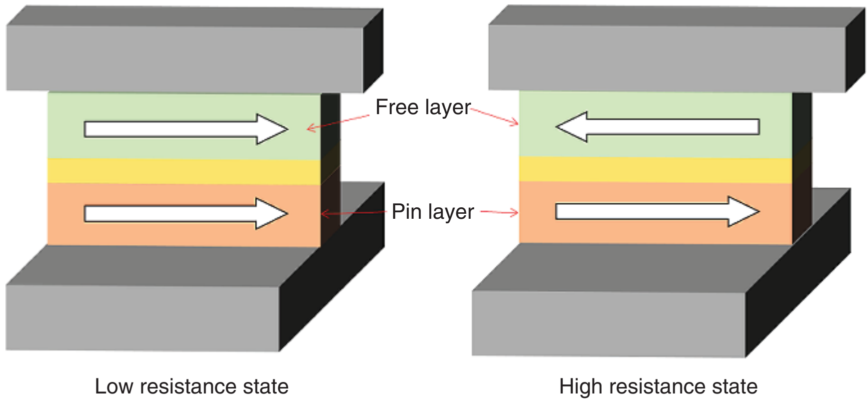


Figure 1.11 Schematic diagram of spin valve structure where arrows indicate the magnetization directions.

materials are rare and are usually strong in one property but very weak in another, such as $BiFeO_3$, which is very strong in ferroelectrics but very weak in ferromagnetic (it is antiferromagnetic in fact). This makes multiferroic materials hard to be practically applied in devices. However, people have been trying to make composite materials such as piezoelectric with magnetostrictive materials, where the mechanical coupling between them makes the "multiferroic" meaningful for device application, for example, making very sensitive magnetic field sensor.

The magnetoelectric (ME) effect is the phenomenon of inducing magnetization by an applied electric field (E) or polarization by magnetic field (H). Many efforts have been devoted to improve the limit of detection of the ME composite at low frequency range, and values of $\sim 10^{-7}$ Oe at 1 Hz has been reported (Wang et al. 2011). Based on the magnetic–strain–electric coupling, scientists have demonstrated dc magnetic field sensor with a detection limit of 2×10^{-5} Oe to dc magnetic field with a nonlinear ME magnetic effect (Li et al. 2017). Ferroelectric material PZT and magnetostrictive material Metglas have been implemented in the composite device (see Figure 1.12).

1.4 Ferroelastic Material and Device Application

Shape memory alloys (SMAs) are the most typical ferroelastic material, which is an important member of ferroics. The shape memory characteristics originates from the phase transition between high temperature austenite phase and low temperature martensite phase, where the shape at cubic-austenite phase can be resumed from low temperature martensite phase whose lattice can be largely twisted (see Figure 1.13).

The SMAs have been widely used in devices from brace of orthodontia and other medical applications, air jet, satellite antenna, etc. Research was carried out in developing systems that would optimize the chevron "immersion"

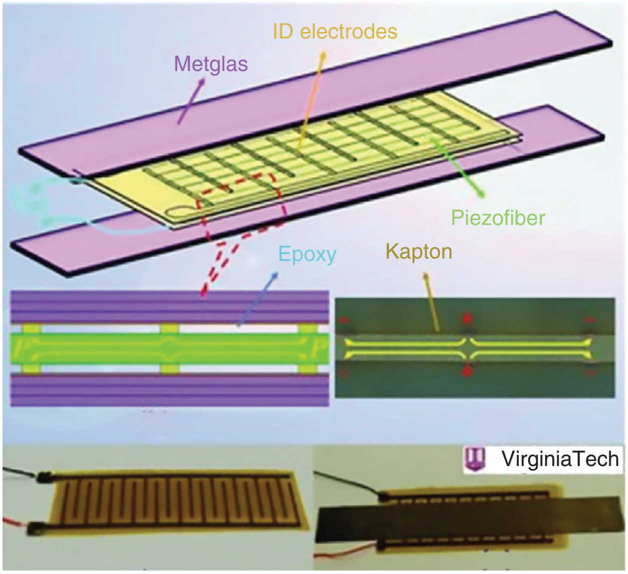


Figure 1.12 Outline of ME device from Virginia Tech and schematic of the cross-section of the ME composite. Source: Wang et al. (2011). Adapted with permission of John Wiley and Sons.

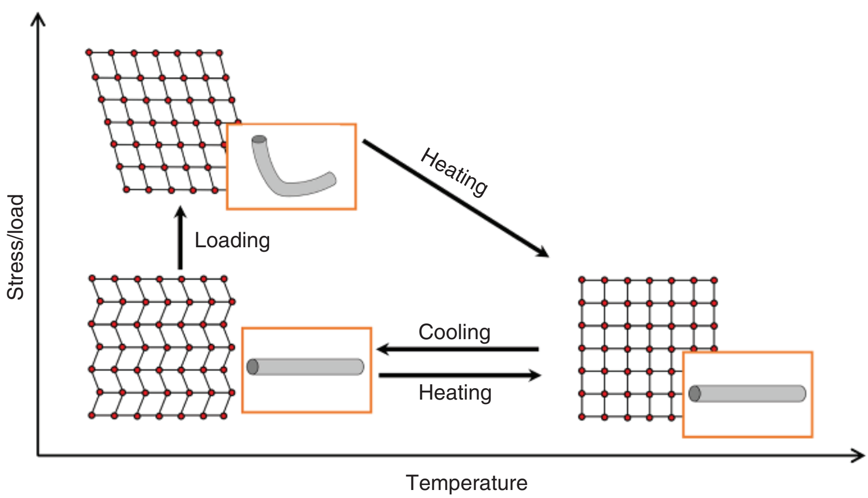
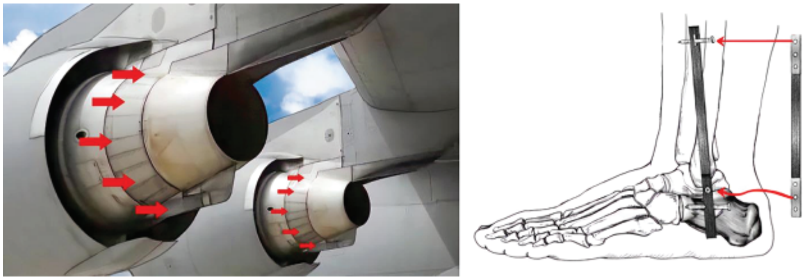


Figure 1.13 Phase transition between high temperature austenite phase and low temperature martensite phase, where the shape at cubic-austenite phase can be resumed from low temperature martensite phase whose lattice can be largely twisted.

into the jet flow based on the flight condition. As shown in Figure 1.14a, SMAs activated by heat were developed that would allow for full chevron immersion in jet flow during high thrust requirements (e.g. during take-off) and not immersing it during cruise where the thrust efficiency is of greater importance (Anon n.d.).



(a) (b)

Figure 1.14 (a) Brace of orthodontia using shape memory alloys and (b) arthrodesis device developed by Karnes et al.

For broken bone rehabilitation, a SMA plate with a memory transfer temperature close to body temperature can be attached to both ends of the broken bone as shown in Figure 1.14b. From body heat, the plate will contract and retain its original shape, therefore exerting a compression force on the broken bone at the place of fracture. After the bone has healed, the plate continues exerting the compressive force and aids in strengthening during rehabilitation (Garlock et al. 2017).

1.5 Scope of This Book

In Chapters 2–5, fundamentals of ferroelectrics, applications of ferroelectric materials, recent advances, and advanced measurement and testing techniques in ferroelectrics will be introduced. In particular, device applications of ferroelectric materials in thin film form will be introduced including FeRAM, ferroelectric tunneling-based resistive switching, etc. The recent advances include ferroelectricity in emerging materials such as 2D materials and high-*k* gate dielectric material HfO_2, while the advanced characterization technologies include the piezoresponse force microscopy (by imaging and switching ferroelectric domains) and Cs-corrected transmission electron microscopy (TEM) where atomic level ionic displacement can be identified.

As the most important property application of ferroelectric materials, fundamentals of piezoelectric physics and engineering considerations for device design and fabrication are introduced in Chapters 6 and 7.

In Chapter 8, starting with a brief introduction on origin of ferromagnetism and its analogy to ferroelectrics, device applications, particularly for magnetostrictive devices, are introduced.

Chapters 9 and 10 will introduce the multiferroics of materials possessing both ferromagnetic and ferroelectric orders including single phase and composite materials. In particular, devices based on the integration of ferroelectric and ferromagnetic materials such as multiferroic memory device and ME coupling device for sensor applications will be introduced.

In Chapter 11, ferroelastic materials represented by SMA and magnetic SMAs as well as their device applications will be introduced.

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