PROCESSING AND CHARACTERIZATION OF PIEZOELECTRIC MATERIALS AND INTEGRATION INTO MICROELECTROMECHANICAL SYSTEMS

Dennis L. Polla
Department of Electrical and Computer Engineering, University of Minnesota, Minneapolis, Minnesota, 55455; e-mail: polla@ece.umn.edu

Lorraine F. Francis
Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota, 55455; e-mail: lfrancis@maroon.tc.umn.edu

KEY WORDS: ferroelectric, MEMS, sensors, actuators

ABSTRACT
Piezoelectric materials have been integrated with silicon microelectromechanical systems (MEMS) in both microsensor and microactuator applications. Thin-film materials selection and processing routes are reviewed. Some recent and emerging applications of piezoelectric MEMS are presented including acoustic emission microsensors, vibration monitors, molecular recognition biosensors, precision positioners, micropumps, and linear stepper motors.

INTRODUCTION
Microelectromechanical systems (MEMS) continues to be an exciting multidisciplinary field with tremendous progress taking place in research and commercialization. MEMS takes advantage of well-established manufacturing methods routinely used in the integrated circuit industry to make intelligent devices and...
systems capable of sensing, actuating, and processing information. MEMS pattern definition methods, commonly referred to as micromachining (1–3), are used to form mechanical structures that are often realized using processing steps compatible with those used to make integrated circuits. In addition, specialized processes, novel materials, and customized packaging methods are routinely used. MEMS themes include miniaturization, multiplicity, and microelectronic manufacturing and integration.

Huge technology opportunities for MEMS are present in automotive applications, medicine, defense, controls, and communications. One common MEMS device in commercial production today is the miniature accelerometer used to control the deployment of an air-bag in an automobile. Several companies manufacture this device based on a variety of physical sensing phenomena. Other applications include biomedical pressure sensors and projection displays. For several excellent MEMS overviews of both core technologies and emerging applications, the reader is encouraged to consult References 4–7.

MEMS can be classified in two major categories: sensors and actuators. MEMS sensors, or microsensors, usually rely on integrated microfabrication methods to realize mechanical structures that predictably deform or respond to a specific physical or chemical variable. Such responses can be observed through a variety of physical detection methods including electronic and optical effects. Structures and devices are designed to be sensitive to changes in resistance (piezoresistivity), changes in capacitance, and changes in charge (piezoelectricity), with an amplitude usually proportional to the magnitude of the stimulus sensed. Examples of microsensors include accelerometers, pressure sensors, strain gauges, flow sensors, thermal sensors, chemical sensors, and biosensors. MEMS actuators, or microactuators, are usually based on electrostatic, piezoelectric, magnetic, thermal, and pneumatic forces. Examples of microactuators include positioners, valves, pumps, deformable mirrors, switches, shutters, and resonators.

The focus of this paper is to review recent progress in the use of piezoelectric thin films in MEMS (8). Although each application of MEMS requires a specific design to satisfy many constraints and conditions, piezoelectric-based MEMS are generally attractive due to their high sensitivity and low electrical noise in sensing applications and high-force output in actuation applications (8, 9). Recent interest in incorporating piezoelectric lead zirconate titanate thin films in MEMS reflects the promise of these materials (8–10, 10a–f).

The physical basis for the design of piezoelectric MEMS is based on simple combined electrical and mechanical relations (Gauss’ law and Hooke’s law). The relationship between the electrical and mechanical properties of piezoelectrics is governed by the following constitutive equations:

\[ S_i = s_{ij} T_j + d_{ik} E_k \]
MICROELECTROMECHANICAL SYSTEMS

\[ D_i = d_{im} T_m + \varepsilon_{in}^T E_n, \]

where \( i, j, m = 1, \ldots, 6 \) and \( k, l, n = 1, 2, 3 \). Here, \( S, D, E, \) and \( T \) are the strain, dielectric displacement, electric field, and stress, respectively, and \( s_{ij}^E, d_{kl}, \) and \( \varepsilon_{ln}^T \) are the elastic compliances (at constant field), the piezoelectric constants, and dielectric permittivities (at constant stress).

MATERIALS

A piezoelectric thin film is at the heart of the piezoelectric MEMS sensor or actuator. An understanding of the development of crystal structure, microstructure, and properties of these films is necessary for the MEMS structural design and process integration. In this section, piezoelectric thin films are reviewed, beginning with a short discussion of piezoelectric materials in general, followed by thin-film processing, structure and property development (focusing on solution deposition routes) and lastly, piezoelectric properties of thin films.

Piezoelectric Materials

A piezoelectric is a material that develops a dielectric displacement (or polarization) in response to an applied stress and, conversely, develops a strain in response to an electric field (11). To achieve the piezoelectric response, a material must have a crystal structure that lacks a center of symmetry. Twenty of the possible 32 point groups that describe a crystal’s symmetry fulfill this requirement and are piezoelectric (12). The importance of the crystal structure to piezoelectricity extends into understanding the constitutive equations describing the piezoelectric’s response (Equations 1 and 2 above). For example, the application of an electric field along a certain crystallographic direction may cause a strain in more than one direction. Such relationships between applied electric field and strain, and between applied stress and dielectric displacement (or polarization), are specific to the piezoelectric’s crystal structure, and the magnitude of the response is given by a material’s piezoelectric coefficients \( (d_{ij}) \). The piezoelectric constitutive relationships are described in detail in several texts (11–13).

A wide variety of materials are piezoelectric, including poled polycrystalline ceramics (e.g. lead zirconate titanate, PZT), single-crystal or highly oriented polycrystalline ceramics (e.g. zinc oxide and quartz), organic crystals (e.g. ammonium dihydrogen phosphate), and polymers (e.g. polyvinylidene fluoride), as shown in Table 1 (14). In general, these piezoelectrics belong to one of two categories: those that are also ferroelectric and those that are not. Ferroelectric materials have the further restrictions that their crystal structures have a direction of spontaneous polarization (10 of the point groups are polar) and that their polarization can be oriented by the application of an electric field and will
Table 1  Properties of some piezoelectric materials (adapted from 14)

<table>
<thead>
<tr>
<th>Material</th>
<th>Formula</th>
<th>Form</th>
<th>Piezoelectric constant (pm/V or pC/N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium dihydrogen phosphate (ADP)</td>
<td>NH$_4$H$_2$PO$_4$</td>
<td>Single crystal</td>
<td>$d_{36} = 48$</td>
</tr>
<tr>
<td>Barium titanate</td>
<td>BaTiO$_3$</td>
<td>Single crystal</td>
<td>$d_{15} = 587$</td>
</tr>
<tr>
<td>Barium titanate</td>
<td>BaTiO$_3$</td>
<td>Polycrystalline</td>
<td>$d_{15} = 270$</td>
</tr>
<tr>
<td>ceramic</td>
<td></td>
<td>ceramic</td>
<td></td>
</tr>
<tr>
<td>Lead zirconate titanate (PZT)</td>
<td>PbZr$<em>{0.5}$Ti$</em>{0.4}$O$_3$</td>
<td>Polycrystalline</td>
<td>$d_{33} = 117$</td>
</tr>
<tr>
<td>ceramic</td>
<td></td>
<td>ceramic</td>
<td></td>
</tr>
<tr>
<td>Lead lanthanum zirconate titanate (PLZT)</td>
<td>Pb$<em>{0.925}$La$</em>{0.075}$Zr$<em>{0.56}$Ti$</em>{0.44}$O$_3$</td>
<td>Polycrystalline</td>
<td>$d_{33} = 545$</td>
</tr>
<tr>
<td>Polyvinylidene fluoride (PLZT)</td>
<td>(CH$_2$CF$_2$)$_n$</td>
<td>Oriented film</td>
<td>$d_{31} = 28$</td>
</tr>
<tr>
<td>Potassium dihydrogen phosphate (KDP)</td>
<td>KH$_2$PO$_4$</td>
<td>Single crystal</td>
<td>$d_{16} = 21$</td>
</tr>
<tr>
<td>Quartz</td>
<td>SiO$_2$</td>
<td>Single crystal</td>
<td>$d_{11} = 2.3$</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>ZnO</td>
<td>Single crystal</td>
<td>$d_{13} = 12$</td>
</tr>
</tbody>
</table>

remain oriented to some degree when that field is removed (15). This property of polarization reversal and remanence cannot be predicted by the material’s structure; it must be determined experimentally. The polarization-field hysteresis loop illustrated and described in Figure 1 is the practical demonstration of ferroelectricity. What importance is the distinction between ferroelectric and nonferroelectric for piezoelectric materials? The ferroelectric’s ability to orient its polarization allows it to be poled (by application of an electric field typically at elevated temperature) so that the polar axes in a random polycrystalline material can be oriented and produce a net piezoelectric response.

The application of piezoelectrics in MEMS requires that the material be processed within the constraints of microfabrication (see the next section) and have the properties necessary to produce a MEMS device with the desired performance. Microfabrication nominally requires that a thin film be prepared with conducting electrodes and that the film be ferroelectric or oriented (textured) properly for the desired piezoelectric response. Fabrication of some devices requires that the film be patterned and that it withstand processes such as encapsulation and wire bonding. Zinc oxide with a preferred orientation fits this first requirement and has been used as piezoelectric film for many years (16) and more recently in MEMS (17). A second consideration is the properties that include the piezoelectric constants, as well as the dielectric properties and
Figure 1  A polarization-electric field hysteresis loop. When a field is applied to a randomly oriented polycrystalline material, domains (regions of uniform polarization) align with respect to the applied field to give a net polarization that saturates at value $P_{\text{sat}}$. When the field is reduced back to zero, a remanent polarization ($P_r$) persists; when the field is applied in the opposite sense, the polarization reduces to zero with the application of the coercive field ($E_c$) and then switches directions and saturates.

elastics properties. The specific property requirements depend on the device, but in general large piezoelectric constants are desired for piezoelectric MEMS. Ferroelectric ceramics, particularly those with the perovskite ($\text{ABO}_3$) structure, are known to have very high piezoelectric constants. The ferroelectric ceramics receiving the most widespread use as bulk piezoelectrics as well as thin-film piezoelectrics are in the lead zirconate titanate ($\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$, PZT) system.

The PZT family of ceramics is widely used due to its excellent piezoelectric and dielectric properties (11). PZT materials have the perovskite structure ($\text{ABO}_3$) in cubic, tetragonal, rhombohedral, and orthorhombic forms, depending on the temperature and composition, as shown in the Figure 2. Extensive research has been carried out to determine the effects of composition ($\text{Zr/Ti}$) and small amounts of additives on the electrical and mechanical properties (11, 18–20). Several important points should be noted. Compositions near the morphotropic phase boundary (i.e. the boundary between rhombohedral and tetragonal phases at $\text{PbZr}_{0.53}\text{Ti}_{0.47}\text{O}_3$) have the largest piezoelectric constants and dielectric constants. This enhancement is due to the greater ease of polarization. These compositions are so common that in this paper PZT is used to refer to compositions close to this boundary. Additives with a donor character (ionic species that substitute on a site of lower valence) increase the resistivity,
but also increase mechanical and dielectric losses. These additives are known as softeners because they decrease the coercive field and elastic moduli; included are La$_2$O$_3$ and Nb$_2$O$_5$, in small amounts ($<2$ mol%). Additives with an acceptor character decrease the resistivity and decrease losses. These additives are called hardeners because they increase the coercive field and elastic moduli; included are Na$_2$O and Fe$_2$O$_3$. Combinations of donors and acceptors may be used. Some additives (e.g., MnO) are used in excess of the solubility limit to form a grain boundary phase that tends to stabilize properties. For bulk PZT, modifiers are incorporated universally to tailor properties; however, only a few studies have been directed toward additive effects in PZT thin films (21).

Several other ferroelectric ceramics have properties that are comparable with those in the PZT system, particularly other perovskite-based ceramics that have morphotropic phase boundaries (MPB). Among those with properties of interest for MEMS are ceramics in the lead magnesium niobate-lead titanate system (MPB at 30 mole% lead titanate) (22), lead zinc niobate-lead titanate system (MPB at 9 mole% lead titanate) (23) and the lead scandium niobate-lead titanate system (MPB at 42 mole% lead titanate) (24). There are also a number of interesting compositions in the lead lanthanum zirconate titanate system (PLZT) (25). However, the list of materials of interest for piezoelectric MEMS does not stop here; the literature on piezoelectric MEMS reveals that two materials have dominated: PZT and ZnO. In this review, we focus on the use of PZT in MEMS devices.

Figure 2  Phase diagram for the PbZrO$_3$-PbTiO$_3$ system (adapted from Reference 11). The nearly vertical phase boundary between the rhomboedral and tetragonal phases is called the morphotropic phase boundary.
Thin-Film Processing, Structural Evolution, and Properties

For piezoelectric MEMS, a key processing challenge is to create a piezoelectric thin film with the desired structure and properties. A revival in research on ferroelectric ceramic thin films began in the early 1980s and has led to significant progress in understanding how to process thin ceramic films and control their electrical properties. This research has been sparked primarily by non-MEMS applications such as FRAMs (ferroelectric random access memories; 26), dynamic RAM (DRAMs; 27) and high dielectric constant decoupling capacitors (28). The knowledge gained in these pursuits benefits piezoelectric MEMS due to the similarities in the materials used. A series of proceedings volumes on ferroelectric thin films provides a host of information on the topic (29, 29a,b). Here we focus on thin-film processing by solution deposition and its implication on the structural evolution of the film and resulting properties.

In processing PZT piezoelectric thin films, several routes are available, including physical vapor deposition, chemical vapor deposition, and solution deposition. Each method has unique advantages and disadvantages. While a complete discussion is beyond the scope of this review, some general statements can be made. Physical vapor deposition routes (e.g. sputtering; 30) and chemical vapor deposition routes (e.g. MOCVD; 31) offer uniform thickness films and good step coverage; in addition, these routes are currently standard in microfabrication facilities. However, depositing the correct stoichiometry from these routes is often challenging. By contrast, solution deposition (described below) offers excellent control of the chemistry of the thin film but is not appropriate when uniform film thickness over surface features is required (32). A further advantage of solution deposition routes is their simplicity (no vacuum or reactor chambers are required). The similarities between solution deposition and processing of photoresist layers also makes implementation in a microfabrication facility possible.

Solution deposition methods have three basic steps: synthesis of a metalorganic solution, deposition onto a substrate by a spin-casting or dip-coating method, and heat-treatment to remove organics and crystallize the ceramic microstructure. The general considerations in processing ceramic coatings by such routes are reviewed elsewhere (33, 34). In addition, several reviews on solution-deposited ferroelectric films can be found in the literature (35–37). For PZT thin films prepared by this processing route, the greatest diversity comes in the choice for the metalorganic solution. Under the umbrella of solution deposition (35) are the sol-gel routes in which a solution that is capable of forming a gel (usually by reaction) is used, metalorganic decomposition (MOD) routes in which nonreactive precursors are co-deposited, and hybrid routes that
involve some reaction between precursors. Many solution deposition routes have been reported; here, two that have been used in our lab are given as examples.

One of the oldest and most popular routes (38) is shown schematically in Figure 3. This route begins with Zr and Ti alkoxides and Pb acetate trihydrate, separately dissolved in 2-methoxyethanol; care is taken to create an anhydrous alkoxide-based solution that is stable over time (so long as it is not exposed to

\[ \text{Zr(O} \text{CO}_3 \text{H}_7)\text{O}_4 \]
\[ \text{Ti(O} \text{CO}_3 \text{H}_7)\text{O}_4 \]
\[ \text{CH}_3\text{OC}_2\text{H}_4\text{OH} \]
\[ \text{Distill off } \text{C}_2\text{H}_5\text{OH} \]

\[ \text{Pb(CH}_3\text{COO)}_2\text{H}_2\text{O} \]
\[ \text{CH}_3\text{OC}_2\text{H}_4\text{OH} \]
\[ \text{Distill off } \text{H}_2\text{O}, \text{ solvent} \]
\[ \text{Redilute and repeat (2)} \]

\[ \text{Zr-Ti Precursor Solution} \]
\[ \text{Pb Precursor Solution} \]
\[ \text{Dopant Solution} \]
\[ \text{React and distill at 128°C} \]
\[ \text{Concentrate and remove reaction products by vacuum distillation, redilute and repeat} \]

1M PZT Solution

\[ \text{a) Solution synthesis and (b) thin film processing for a sol-gel method based on 2-methoxyethanol.} \]
moisture). As shown below for a generic metal alkoxide \([\text{M(OR)}_n]\), the addition of water leads to hydrolysis (Equation 3) and condensation reactions (Equations 4 and 5) that form larger molecular weight oligomers and eventually a gel (i.e. an interconnected solid structure with a liquid phase interspersed) (34).

\[
\text{M(OR)}_n + \text{H}_2\text{O} \rightarrow (\text{RO})_{n-1}\text{M(OH)} + \text{ROH}, 
\]

3.

\[
(\text{RO})_{n-1}\text{M(OH)} + \text{M(OR)}_n \rightarrow (\text{RO})_{n-1}\text{M-O-M(OR)}_{n-1} + \text{ROH}, 
\]

4.

\[
(\text{RO})_{n-1}\text{M(OH)} + (\text{RO})_{n-1}\text{M(OH)} \rightarrow (\text{RO})_{n-1}\text{M-O-M(OR)}_{n-1} + \text{H}_2\text{O}. 
\]

5.

For coating preparation, some water is added prior to deposition to adjust viscosity and wetting behavior as well as to begin the reaction. One of the many alternative routes is shown in Figure 4 (39, 40). Here a Ti alkoxide is first reacted with acetic acid and water to form an oligomer; then this Ti precursor is combined with Zr and Pb precursors. Unlike the previous case, this solution’s chemistry and properties vary with time, and the variation must be understood to achieve the appropriate microstructure and properties in the PZT film. However, this disadvantage is balanced by the ease and speed of the solution synthesis and the use of water as one of the main solvents. The steps taken after solution synthesis to prepare the final crystalline ceramic coating are also somewhat different between the two routes. Because each solution deposition route has a unique viscosity, concentration, and chemistry, individual layer thicknesses and organic contents vary; hence, the drying and thermal treatment steps must be tailored.

The development of crystal structure, microstructure, and properties is strongly dependent on processing conditions such as the solution chemistry, the thermal treatment and the gas atmosphere, as well as the electrode onto which the film is deposited. The first challenge in structural development is to form the desired perovskite crystal structure and eliminate the metastable pyrochlore (or fluorite; 41) form. On heating, pyrochlore forms at a lower temperature than does perovskite (42–44) and is a common alternative form for many perovskite ferroelectrics, particularly relaxor ferroelectrics. Because this pyrochlore is nonferroelectric and has a low dielectric constant, both the ferroelectric and dielectric constant are degraded by its presence (43). For PZT, pyrochlore will transform into perovskite when the film is heated to higher temperatures (42–45). In many cases, pyrochlore is found preferentially at the surface and goes undetected in X-ray diffraction. Surface pyrochlore may also be indicative of lead oxide evaporation (42, 46). In nearly all processing schemes, excess lead is added to solutions to accommodate the evaporation and combat pyrochlore formation. This excess also has been shown to enhance the formation of perovskite and improve properties (42), as well as lower the temperature of
**Figure 4**  
(a) Solution synthesis and (b) thin-film processing for a water-based solution decomposition route (adapted from Reference 39).
perovskite crystallization in PZT (47) and PbTiO$_3$ (48). Another way to combat lead loss is to use a lead oxide overcoat (46, 49). For both methods, care must be taken to avoid the persistence of lead-rich phases in the film, as these can degrade properties.

The solution chemistry affects the degree of association between the chemical species in the complicated multicomponent system and therefore has a dramatic effect on phase development. An ideal situation would be a well-controlled stoichiometric metalorganic precursor molecule, such as a heterometallic alkoxide (50). While this approach has proven successful for a simpler two-component oxide, LiNbO$_3$, (51, 52), the pursuit is more challenging for PZT (53). Even when a single well-bonded precursor is not possible, steps can be taken toward achieving molecular level mixing. For example, Lakeman & Payne (54) show the impact that removal of acetate by-products has on crystalline phase development and microstructure in thin films prepared by the methoxyethanol route (similar to Figure 3). In the water-based route (Figure 4), the extent of molecular mixing and reaction in solution was found to vary with time after the initial synthesis (before deposition), and this variation affected crystal structure and microstructure development, as shown in Figure 5. Many other examples relating a change in solution chemistry to a change in microstructure or properties have been reported. Schwartz et al (55) propose that some of the changes in film microstructure can be linked to changes in film pyrolysis, which are influenced by solution preparation conditions.

Thermal treatment conditions also impact the crystalline phase development. Thermal treatments usually consist of at least two steps (usually after drying): one to remove residual bound organics (and, sometimes, solvent) and another to develop the perovskite microstructure. The two-step procedure can be performed on a single layer after deposition or after several layers have been deposited. Figure 5 shows SEM micrographs of PZT thin films prepared by a water-based solution deposition route (Figure 4). (a) A film prepared from an optimized solution and (b) a film prepared with solution conditions not optimized. The arrow points to a region of surface pyrochlore (adapted from Reference 39).
deposited. The first step may not only remove organics but also lead to some pyrochlore crystallization. For PZT, this initial pyrochlore does not prevent complete transformation to perovskite, but in other materials such as lead magnesium niobate, a single heat treatment to high temperature is a better route so that the pyrochlore formation can be minimized (56). The effect of heating rate, including rapid thermal processing (57, 58), has been explored. An interesting and unexpected effect of thermal treatment on structure was reported by Chen & Chen (59). They showed that films prepared by an MOD route and deposited on Pt-coated Si form perovskite with a [111] texture when rapidly heated to 600–700°C, whereas a two-step treatment leads to [100] texture. The result was attributed to the heteroepitaxy of a Pt$_{5–7}$Pb intermetallic phase that formed at the Pt/film interface during the rapid heating treatment. One persistent challenge is to lower the temperature for perovskite formation; depositing the PZT film onto a thin layer of crystalline lead titanate improves the nucleation of the perovskite phase and reduces the processing temperature by 100°C (60, 61).

The electrode or substrate is as important as any processing condition in determining the structure and properties of the film. The electrode materials of choice for integration with Si are platinum (with a thin Ti adhesion layer) (62–65) and conductive oxides such as RuO$_2$ (65, 66) and LaNiO$_3$ (67). Typically these layers are part of a larger electrode stack that is also designed to prevent interdiffusion (see below). The electrode material has the most profound effects on the fatigue characteristics of ferroelectric thin films designed for FRAM applications; oxide electrodes provide much better polarization retention (65). Electrodes also potentially impact the crystalline structure through providing nucleation sites and influencing orientation. For example, the close lattice match between (111) Pt and (111) PZT can influence the film texture. Substrates also play a role. Tuttle et al (68) showed that substrate thermal expansion coefficient influences the stress-state of the film and the resulting crystallographic orientation and switching properties. They found that solution deposited films on Pt-coated MgO were in a state of compression, whereas those deposited on Si-based substrates were in tension.

In optimized solution–deposited PZT films, the dielectric and ferroelectric properties typically are comparable to those of bulk ceramics. For example, a ferroelectric hysteresis loop for a PZT thin film is shown in Figure 6. Structural factors, especially crystallographic orientation, presence of point defects, film thickness (in some cases), and interfacial phases do have important effects on properties. For example, the remanent polarization in a c-axis oriented PZT film has been shown to reach 50 µC/cm$^2$ (69). Oxygen vacancies at the electrode/ferroelectric interface are believed responsible for voltage offsets in hysteresis loops (70). Additionally, several researchers (56, 71) have discussed the effect of a thin, low dielectric constant interfacial phase on dielectric properties.
Ferroelectric and dielectric structure-property relationships in thin films are better understood due to the tremendous research effort in the past decade. Less understood are the piezoelectric structure-property relationships. Since these are central to piezoelectric MEMS, they are discussed in greater detail below.

**Piezoelectric Properties and Characterization**

The piezoelectric response in thin films can be measured by applying a stress to the film and measuring the induced charge (direct effect) or by applying an electric field and measuring the strain induced in the film (converse effect). For PZT thin films, the piezoelectric constants of interest are $d_{33}$ and $d_{31}$. The first ($d_{33}$) relates the strain ($S_3$) in the direction of electric field ($E_3$) to the electric field strength ($S_3 = d_{33}E_3$) or equivalently relates the induced charge ($D_3$) on electroded faces perpendicular to an applied stress ($T_3$) to the stress ($D_3 = d_{33}T_3$). The second ($d_{31}$) relates the strain ($S_1$) in the direction perpendicular to the applied field to the field strength ($S_1 = d_{31}E_3$) or relates the induced charge on electrodes parallel to the direction of stress application to the stress ($D_3 = d_{31}T_1$). The piezoelectric effect has been detected in poled and unpoled films. Without poling, a preferred crystallographic orientation, as well as possible alignment during measurement, makes this response possible. Poling requires application of an electric field, typically at higher temperatures, to align domains and develop a net polarization in a polycrystalline film. A considerable amount of research is now underway to try to understand the piezoelectric properties of thin-film ceramic ferroelectrics such as PZT.

![Ferroelectric hysteresis loop](image)
For the direct effect, a normal load can be applied onto an electroded piezoelectric film and the charge on the electrodes measured. In this case, the electrical response is parallel to the applied stress and a $d_{33}$ coefficient is determined. For example, Lefki & Dormans (72) applied loads up to 10 N to a 1 mm$^2$ area and determined the induced charge by measuring the voltage drop across a capacitor in parallel. For $d_{31}$ determination, a stress in the plane of the film can be applied (e.g. by flexing a substrate coated with a piezoelectric layer) and the induced charge measured (73).

For the converse effect, an electric field is applied and a strain in a thin film is measured. For $d_{33}$ determination, laser interferometry methods are used to monitor changes in thickness in a film (on a substrate) upon application of a small ac field (74, 75). The technique has excellent displacement resolution ($10^{-2} - 10^{-4}$ Å) and allows characterization of the complex, frequency-dependent piezoelectric properties as well (75). Elimination of possible contributions of bending to the displacement is possible when a double-beam interferometer is employed (76). Determining $d_{31}$ by a converse method requires that the film be prepared as a free-standing thin cantilever beam, sandwiched between two electrodes and anchored on one end (69) or that the film can be deposited on a thin support material (77). The strain in the free-standing film (or bending of a coated beam) is measured as an electric field is applied and used to calculate $d_{31}$, provided that one knows the elastic modulus of that layer.

Like other properties, the piezoelectric properties of PZT thin films depend on structural factors. For example, the presence of a nonpiezoelectric phase (e.g. pyrochlore) dilutes the piezoelectric response. However, unlike the dielectric and ferroelectric properties of thin films, the measured values for the piezoelectric coefficients are typically lower than those of bulk PZT (see Table 2), and dynamics of domain orientation and switching appear to be more complex in films. One observation is that the piezoelectric response (as determined from a small ac electric field) improves with the application of a dc electric field. This effect is illustrated in Figure 7 for behavior of an unpoled film (CR Cho & LF Francis, unpublished results). The enhancement of piezoelectric constant with field and shape of this response can be explained by its coupling to the dielectric constant and polarization, both of which are field dependent (79). Kholkin et al (80) show a similar dependence of $d_{33}$ on the dc bias but display it in a form that emphasizes the polarization reversal occurring during the measurement. The improvement in $d_{33}$ values under dc field can also be related to changes in the polarization state (alignment). When the dc field is removed (see Figure 7), the piezoelectric response improves relative to its initial (unpoled) state, but is still significantly lower than the value under high field. Several possible reasons account for the lower $d_{33}$ in films compared with bulk: stress in the film, substrate constraint (72), and higher probability of reorientation of
Table 2  Reported piezoelectric constants for PZT thin films with compositions near the morphotropic phase boundary

<table>
<thead>
<tr>
<th>Processing route</th>
<th>Measurement</th>
<th>Poling conditions</th>
<th>Piezoelectric constants (pm/V or pC/N)</th>
<th>Reference</th>
</tr>
</thead>
</table>
| Solution deposition | Direct-normal load | Unpoled ~200 kV/cm for a few min | d_{33} = 0  
d_{33} = 400 | 72 |
| MOCVD | Direct-normal load | Unpoled ~40 kV/cm for a few min | d_{33} = 20–40  
d_{33} = 200 | 72 |
| Solution deposition | Direct-flexed substrate | 200 kV/cm for 21 h | d_{31} = −77 | 73 |
| Solution deposition | Converse (single beam interferometer, dc bias) | Unpoled | d_{33} = 80 | 75 |
| Solution deposition | Converse (double beam interferometer, dc bias) | Poled 230 kV/cm, 900 s | d_{33} = 58 | 81 |
| RF Magnetron sputtering | Direct (free-standing film beam deflection) | Unpoled (c-axis oriented) | d_{31} = −100 | 69 |
| Solution deposition | Converse (single beam interferometer, dc bias) | Unpoled | d_{33} = 80 | 78 |
| Solution deposition | Converse (single beam interferometer, no dc bias) | Unpoled | d_{33} = 27 | 39 |
| Solution deposition | Converse (double beam interferometer, dc bias) | ? | d_{33} = 100  
(0.33 µm thick)  
d_{33} = 140  
(7.1 µm thick) | 80 |

domains when the field is removed. The fact that substrate constraint will lower the measured response has led some researchers to use the term effective $d_{33}$ (72, 80).

Poling the film usually improves the piezoelectric response, but the results depend on the specific poling conditions (field strength, temperature, time), as well as the time after poling the measurement is taken (see Table 2 for examples). In a detailed study, Khoklin et al (81) showed that the $d_{33}$ value of a PbZr_{0.45}Ti_{0.55}O_3 film freshly poled at room temperature drops with time after poling, but this effect is minimized when longer poling times are used.
Increasing the poling temperature from room temperature to 140°C was reported to increase the $d_{33}$ of a PbZr$_{0.45}$Ti$_{0.55}$O$_3$ film from $\approx 46$ to $\approx 56$ pC/N; the better performance for higher poling temperature was attributed to an internal bias field.

Structural factors, including crystallographic orientation, grain size, presence of second phases at interfaces, and film thickness, as well as the composition of the piezoelectric, influence the piezoelectric properties of thin films. Research on these effects is in progress and will be significant for the further application of piezoelectric ceramic thin films in MEMS. At present, the piezoelectric effect in these films has been demonstrated to be sufficient for MEMS applications (see below).

**INTEGRATION ISSUES**

For MEMS applications, the piezoelectric thin film must be integrated into a device with a well-designed physical structure and with a substrate (typically Si) that provides electronic functions. The physical structure of the device should be designed to maximize the sensor response or actuator force (or displacement) output. Often the design entails a combination of the piezoelectric thin film and a flexible support. For example, a PZT thin film (sandwiched between electrodes) on a flexible membrane is a more effective pressure sensor than a PZT film on a solid substrate because the flexing of the membrane allows a contribution to the induced charge through strain in the plane of the membrane.
The electronic functions necessary for MEMS are integrated circuits (ICs) fabricated into the Si substrate. The on-chip electronics provides amplification, signal processing, and diagnostic functions, as well as feedback between sensors and actuators that may be located on the same chip. Integration of the piezoelectric thin film must then be compatible with the fabrication of complex device structures and supporting electronics. Consequently, the challenges to integration and fabrication of piezoelectric MEMS are many. In this section, a brief overview of a typical fabrication sequence is given, highlighting the important integration issues.

Figure 8 shows an overview of the main processing stages used to fabricate a cantilever beam-based microsensor. The detailed sequence of processing steps entails over 50 individual operations and a wide variety of microfabrication technologies. The main fabrication stages are the construction of a region of sacrificial material; the deposition of a structural material, electrodes, and piezoelectric on top of that; and lastly the removal of the sacrificial material to make a free cantilever MEMS structure. The first stage in the fabrication sequence is recessed trench formation.
sequence is not represented in Figure 8, i.e. fabrication of on-chip electronics, such as CMOS circuits for amplification. Because the piezoelectric material is considered a contamination risk, the IC fabrication precedes the construction of the MEMS device (83). The circuit is protected by an encapsulating layer while the MEMS is processed, and in a final step, metal connections are made between the circuit and the MEMS device. Of concern is the influence of the high-temperature processing of some of the MEMS materials on the dopant profiles and performance of the IC transistors. With typical conditions, an adequate thermal budget can be designed to avoid problems.

In this fabrication example, surface micromachining is used to create the free-standing three-dimensional surface structure. The technique involves depositing a structural material on top of a sacrificial material that is later removed by selective etching (84). Bulk micromachining is an alternative method of fabrication in which the three-dimensional structure is formed by etching a bulk Si crystal (or other substrate), making use of anisotropic etch rates. Surface micromachining has been employed to make a variety of MEMS devices and has advantages over bulk micromachining in many cases. In surface micromachining, the Si wafer retains mechanical strength and is more available for on-chip electronics and unlike bulk micromachining does not require bonding to another material to define cavities (e.g. for micropumps) (85). The sacrificial material in the surface micromachining process must have structural integrity during processing and good etching characteristics; commonly used are phosphosilicate glass (PSG) prepared by low-pressure CVD (LPCVD) and silicon dioxide (deposited by LPCVD or thermally grown SiO₂). Structural materials of choice are polycrystalline Si and silicon nitride; both can be prepared by LPCVD and with low stress. Other unique combinations of sacrificial and structural materials have been proposed (e.g. sacrificial copper and structural polyimide; 86), but the thermal processing required for the PZT layer limits the choices.

Between the structural material and the piezoelectric thin film is a lower electrode stack composed of a series of layers, each with an important function. The piezoelectric must be deposited on a conducting electrode, most commonly Pt (as discussed above). Unfortunately, Pt cannot be deposited directly onto the silicon nitride or polysilicon structural material due to problems with adhesion and silicide formation during the thermal treatment needed for the piezoelectric (87). In addition, Si diffusion from the structural material into the ferroelectric layer leads to pyrochlore formation (48). To prevent such diffusion and reaction, a barrier is incorporated, but unlike barriers designed for FRAMs and other applications, the barrier thickness in these deforming MEMS structures must be kept to a minimum so that response is not compromised (88). We have found that a very thin layer of titanium dioxide formed in situ during sputtering...
prevents both platinum silicide and pyrochlore formation. Layers to promote adhesion are also needed. If silicon nitride is the structural material, a thin layer of polysilicon promotes adhesion to the titania barrier layer. A thin layer of Ti promotes Pt adhesion to the titania. This lower electrode stack is just one example of a multilayer structure designed to link the structural material to the piezoelectric and provide a conducting electrode.

After deposition of the piezoelectric and upper electrode, the next step is patterning of the electrodes and PZT layer. Reactive ion etching (RIE) in a top-down process is most often used in our laboratory in order to avoid contamination of the PZT. In RIE, material removal is accomplished by a combination of physical (ion bombardment) and chemical (reaction with the etch gas) processes. In their review of dry etching of ferroelectric thin films, Menk et al (89) indicate that RIE is the preferred dry method due to its high etch rate and good anisotropy. Potential drawbacks include etching-induced damage from the ion bombardment and the accumulation of residue on the film. Interesting alternative patterning techniques for solution deposited coatings are currently under investigation. Several researchers have described the use of photosensitive solution precursors (90, 91) or incorporating photosensitive polymers in the solution (92); patterning is accomplished by UV irradiation followed by removal of unexposed material and then thermal treatment. Self-assembled monolayers have also been employed to pattern solution-deposited thin films (93).

The final step in the fabrication is the removal of the sacrificial material by chemical etching, typically in aqueous hydrofluoric acid solution or gas. Since PZT will also be attacked by this treatment, encapsulation with a protective layer of sputter-deposited chromium or LPCVD silicon nitride is needed. Alternatively, a double-coated, hard-baked photoresist can be used (94). For some MEMS devices, special ports are opened in the encapsulated device and channels created to allow the acid to penetrate under membranes. When the sacrificial material is removed, care must be taken to prevent sticking of the freed device to the bottom of the well. Exchange of the aqueous-based etchant with a nonaqueous, lower-surface tension liquid alleviates many sticking problems. Alternatively, ridges can be built into the bottom well surface to limit the contact area (95). After freeing, the devices are ready to use as sensors or actuators.

SENSORS

Microsensors based on piezoelectric thin films have been demonstrated for force measurement, acoustic emission detection, acceleration measurement, biosensing, and other applications. Rather than extensively reviewing the large variety of MEMS-based microsensors that have been realized using piezoelectric thin films, only a few case examples are presented.
Acoustic Emission Microsensors

Acoustic emission (AE) microsensors have been formed using PZT thin films and electrodes deposited directly on a silicon substrate (96). This basic capacitor structure is designed to form a small high frequency (50 KHz, 2 MHz) listening device to detect precursor crack initiation and propagation acoustic emission signatures prior to catastrophic failure of critical aircraft components. The thin PZT films of 0.5 to 1.0 µm thickness are selected for overall compatibility with on-chip silicon electronics and batch processing methods. The silicon-based sensor and pre-amplifier are directly attached by adhesive bonding to a mechanical component of interest. Because the aircraft environment is usually both acoustically and electrically noisy, signal processing is of an equal challenge to developing the acoustic emission sensors. Figure 9 shows a representative cross section of a piezoelectric acoustic emission sensor, and an optical die photograph for a 200 µm diameter sensor is shown in Figure 10.

The overall strategy of microsensor structural health monitoring, using acoustic emission sensors, vibration monitoring devices, and electronics integration, is shown in Figure 11 (97).

Microfabricated piezoelectric AE sensors were tested to confirm responsivity to simulated cracking events. A microsensor package was mounted with a thin
epoxy layer directly to a flat surface of a CH-46 pitch shaft housing. A No. 2 mechanical pencil lead breakage test was used to simulate microcracking. Light banging with a hammer was also used. Figure 12 shows an AE signal (displayed as amplified voltage versus time) detected by a microfabricated sensor under the best conditions of minimizing electromagnetic interference (EMI). The signals

---

**Figure 10** SEM micrograph of the surface of a PZT thin film AE microsensor (400 µm diameter).

---

**Figure 11** Structural health monitoring of critical aircraft components using a 1 cm² silicon microchip containing acoustic emission microsensors, signal conditioning electronics, and telemetry.
Figure 12  Comparison of responses to simulated fracture in a microfabricated AE sensor with a commercial Physical Acoustics Model S9220 non-MEMS sensor.

measured were approximately 0.25 to 0.5 pC (or 50 to 100 µV) in peak amplitude without external pre-amplifier gain. Several additional experiments were carried out using external electrical high-pass filtering techniques to eliminate audio signals in the 20 Hz to 40 kHz range, as well as varying the location of the signal source with respect to the microsensor location.

The results of these experiments demonstrate (a) functionality of microfabricated piezoelectric AE sensors in detecting high-frequency acoustic signals (40 kHz to 2 MHz), (b) the need for integrated AE microsensors with sensor and pre-amplifier located on the same chip or hybrid connected with short wire bonds, and (c) successful signal coupling through the interfaces of the attachment epoxy, ceramic package, and silicon substrate.

Piezoelectric Vibration Monitors

The real-time detection of extraordinary vibration may provide important information in a failure prediction algorithm for a particular system. Rotating machinery typically has characteristic periodic waveforms associated with normal operation, with abnormal waveform components associated with bearing wear, friction, slippage, and particulate debris. The ability to sense in real-time these characteristic signatures is also important to avoid costly damage due to prolonged operation.

Vibration microsensors (98) were fabricated using piezoelectric thin-film microsensors similar to those used in the acoustic emission microsensor discussed above. A main fabrication difference for the vibration microsensor is the need
to have a free-standing cantilever oscillate in response to vibration signals. This requires the use of solid state micromachining techniques to form a deformable microbeam as outlined in Figure 8.

Under ordinary operation, the microfabricated cantilever beam has both a forced response characteristic of the driving excitation and a natural response characteristic of the electro-mechanical resonance of the composite microbeam. The superimposed waveforms derived from multiple vibratory components make signal processing a challenge, and therefore we are currently pursuing a variable length microbeam design and signal processing algorithms to obtain a more complete spectrum of the various vibration components.

Figure 13 shows a scanning electron micrograph of a cantilever microbeam that spontaneously generates a charge when under the influence of forced vibrations derived from rotating machinery. The resonant frequency of the microbeam can be approximated using a first-order analysis assuming a homogeneous stress-free cantilever microbeam (99).

$$f_o = 0.16 (E_Y \rho)[h/L^2]$$.

where $E_Y$ is the effective Young’s modulus, $\rho$ is the density of the microbeam, $h$ is the microbeam thickness, and $L$ is the free-standing microbeam length. For the silicon nitride structural support, microbeam accelerometer/vibration monitors were used; the resonant frequencies are above 100 GHz.

Figure 14 shows the response of a single microcantilever to a calibrated 5.0 g acceleration. Figure 15 shows the natural response of the microcantilever to an impulse event simulating a mechanical impact. In all applications, on-chip signal processing is important in minimizing sensor interconnection losses.
Figure 14  Spectrum analyzer output showing a 5 g signal.

Molecular Recognition Biosensors

A piezoelectric microcantilever beam has been fabricated for the detection of viruses (100). This device uses the same micromachining process as the vibration monitoring devices above but incorporates an additional selective molecular recognition coating on the tip of the cantilever beam. Upon exposure to a conjugate biomolecule, the effective mass at the end of the cantilever changes, and there is a corresponding downward shift in resonant frequency. This change in mass can therefore be sensed by electronically detecting the change in resonant frequency or the amplitude of vibration. A second detection mode relies on the

Figure 15  Natural frequency response of a piezoelectric microcantilever to a mechanical impulse.
detection of a conformational stress in a thin-film coating on the surface of the microcantilever. The temporary strain developed in the cantilever transfers a stress to the underlying piezoelectric thin film. A spontaneous charge is rapidly produced. Upon full biomolecular binding on the surface, the reaction stops, and the induced charge undergoes a natural decay set by the dielectric loss of the piezoelectric material.

Although several applications of the molecular recognition microcantilever are being developed, it appears that this type of MEMS biosensor is extremely sensitive to the detection of molecular binding in genetic testing, the detection of environmental pathogens, and the detection of viruses. Figure 16 shows the cross section of one type of biomolecular microcantilever; a device micrograph is shown in Figure 17.

The biosensor voltage response of the microcantilever to strepavidin (1 mg/mL) binding is shown in Figure 18. The specific binding induces a stress in a polydiacetylene polymer overlying the microcantilever. This stress is transduced to a piezoelectric sensor structure and a corresponding charge (or voltage) is produced. An amplifier detects the piezoelectric response and a characteristic biochemical binding signature is produced. The response time ($\approx 1$ ms) depends on the biochemical reaction kinetics and the electrical characteristics of the piezoelectric microsensor. After all binding sites have reacted, charge leakage of the piezoelectric capacitor is observed, as shown.

Figure 16  Cross section of a molecular recognition biosensor based on piezoelectric thin films.
The piezoelectric device is capable of ultrahigh-sensitivity detection of several human viral pathogens, including influenza and rhinovirus. Testing of this device has revealed its remarkable characteristic to function is air, atomized aerosol, and submerged in a liquid. Application of this device to patient care includes environmental monitoring of filtered air and possibly the measurement of potential pathogens in administered blood products and drugs.

Figure 17 Micrograph of a gold-biotin-coated molecular recognition piezoelectric microcantilever beam.

Figure 18 Response of a biotin-coated piezoelectric microcantilever to binding with strepavidin.
ACTUATORS

Piezoelectric microactuators are based on volumetric expansion associated with the converse piezoelectric effect. Although piezoelectric forces are among the highest demonstrated in MEMS-based actuators, their displacements are relatively small. Because both elastic strain limits and dielectric breakdown strength of the piezoelectric material are considerations in the design of these actuators, most devices demonstrated to-date show a limitation in dielectric breakdown that takes place at electric fields between 0.6 and 1.1 MV/cm.

Micropositioners

Micropositioning actuators using the converse piezoelectric effect have been demonstrated in PZT thin films. The basic device shown in Figure 19 is formed in a geometry of \( N \) piezoelectric bars connected in a meander line configuration that is mechanically in series and electrically in parallel \((101)\). Each bar has electrodes on the two opposing faces parallel to the length of the bar with electrical connection made to the terminals of a dc variable power supply. The piezoelectric polarity between bars is alternated to achieve approximately linear expansion and contraction in adjacent bars. Because both ends of the meander line are anchored to a silicon substrate, the center of the meander line experiences a forward displacement equal to \( N \) times the change in length of a single piezoelectric bar. An additive displacement is therefore obtained. The folded geometry allows a substantial displacement to be obtained on a microfabricated chip.

The force output \( F_{pz} \) obtained from the meander line has been derived by Robbins \((102)\) as

\[
F_{pz} = 2E_Y d_{31} W V,
\]

where \( V \) is the applied voltage, \( W \) is the width of the piezoelectric bar, \( d_{31} \) is the piezoelectric constant, and \( E_Y \) is Young’s modulus.

A microfabricated piezoelectric positioner is shown in Figure 20. Initial results shown in Figure 21 obtained for this device are currently encouraging. Linear displacements have been achieved in the range of 0–4 \( \mu \)m. Problems have been encountered in the fabrication of this device because of the long

Figure 19  Diagram of a MEMS-based folded piezoelectric micropositioner.
effective length over which mechanical integrity of the structure is to be maintained. This is usually characteristic of lateral micromachining steps, which must dimensionally undercut more than 500 µm of material.

**Micropumps**

Piezoelectric thin film, peristaltic micropumps have been fabricated by micromachining silicon nitride structural supports over 2–3 µm deep trenches (Figure 22). These micropumps are currently being developed for the dispensing of small amounts (nL to µL) of chemical reagents needed for biochemical analysis procedures such as those used in genetic testing. The piezoelectric micropump consists of input and output ports micromachined in the top surface of a 500 µm thick silicon wafer. Input and output piezoelectric diaphragms

![Figure 21](image-url) Linear positioning versus applied voltage derived from the meander line device in Figure 20.
Figure 22  Cross section of a piezoelectric peristaltic micropump.

(400 μm diameter) formed over a fluid delivery trench prevent the unwanted movement of fluid through the device. A central diaphragm of 400 μm diameter is used to displace the liquid in either the left or right direction depending on the activation state of the two check valves (Figure 23).

Three-phase pumping action up to 800 Hz has been demonstrated with water. Other more viscous chemicals including blood have difficulty in being forced through the narrow height of the micromachined capillaries. The use of surface coatings and surfactants is currently being evaluated.

Figure 23  Photograph of a piezoelectric peristaltic micropump with output check valves activated by 25 V in the down position. The concentric circles indicate that the three diaphragms have reached the bottom of the micromachined fluid delivery trench under the activation condition.
Linear Stepper Motors

MEMS-based linear piezoelectric stepper motors have been developed for precision positioning applications where high force output and large displacements are required (103). The basic geometry for the stepper motor is shown in Figure 24 and consists of the following key parts: (a) fixed base wafer, (b) segmented clamp wafer, (c) piezoelectric bar, (d) inertial mass, and (e) load interconnect bar. The clamping force between the base wafer and the clamp wafer is the electrostatic attraction between the two wafers (the intervening thin dielectric layer is not shown) when a high voltage is applied between them. On-chip control and drive electronics, telemetry circuits, and other MEMS components can be fabricated on either of the two wafers. A single displacement step is accomplished via a sequence of operations sometimes termed inchworm operation (illustrated in Figure 25) (104). Although the electrostatic clamp is off during the fast PZT expansion step, the external force will not cause any significant movement of the translation stage because the recoil force (which opposes the applied force) of inertial mass will be significantly larger than the applied force. The average speed of translation is proportional to the number of steps taken per unit time. One version of this device has been used in ophthalmic surgery, where forces up to 20 N and translation speeds of up to

Figure 24  Schematic of a piezoelectric linear micromotor.
Three-step operation of the piezoelectric micromotor resulting in a net 1–2 micrometer displacement.

4 mm/s are achieved. This application has served as a technology driver that has led to well-developed high-reliability medical instruments and manufacturing processes. A photograph of a piezoelectric inchworm micromotor is shown in Figure 26.

Simple idealized theoretical models for the stepper have been developed and verified by experimental measurements. By ignoring the effects of static and dynamic friction effects both in the motor and the load (zero friction when the clamp is off and infinite friction when the clamp is on); neglecting the mass of the PZT bar and clamp; considering the load as a constant force with no inertial dependence (i.e. quasi-static operation); and assuming a stepping frequency of \( f_s \), the following equations for the performance of the motor can be derived (WP Robbins, in preparation).

\[
\text{Step size } \delta d = \frac{F_{pzt} - F_A}{k} = \frac{d_{13}LV}{2Y} - \frac{LF_A}{2Ywt}; \quad \text{motor velocity } = \delta df_s. \quad 8.
\]

\[
\text{Motor power consumption (output) } = F_Af_s\delta d = F_Af_s\left\{ \frac{d_{13}LV}{2Y} - \frac{LF_A}{2Ywt} \right\}. \quad 9.
\]
Figure 26 Optical photograph of MEMS-based piezoelectric stepper motor in a customized package for tuning of an NMR spectrometer.

CONCLUSIONS

Piezoelectric materials have been successfully applied in a variety of MEMS applications, including acoustic emission sensors for structural health monitoring, vibration monitors (accelerometers), biosensors, precision positioners, peristaltic micropumps, and inchworm stepper motors. Microactuators and microsensors are designed to make use of the strong piezoelectric response of piezoelectrics such as PZT and to ease the fabrication and incorporation of on-chip electronics. The development of fabrication methods such as surface micromachining, low-stress silicon nitride deposition, and solution deposition of ferroelectric thin films has been essential. The MEMS applications described here compare favorably with other MEMS approaches based on commonly used piezoresistive sensing and electrostatic actuation. The continued promise for piezoelectric MEMS is attractive.

ACKNOWLEDGMENTS

This research was supported by the Office of Naval Research (N00014-95-1-0539) and the University of Minnesota Microtechnology Laboratory Foundation. The authors thank Profs. WP Robbins and RC McGlennen for ongoing collaborations, Drs. S Zurn and GT Cibuzar for help in microfabrication, and
present and former students in the MEMS Center at the University of Minnesota for their efforts in the research presented here.


Literature Cited

35. Tuttle BA, Schwartz RW. 1996. MRS Bull. 21:49–54
42. Tuttle BA, Schwartz RW, Doughty DH, Voigt JA. 1990. See Ref. 29, pp. 159–65
47. Bernstein SD, Kisler Y, Wahl JM, Bernacki SE, Collins SR. 1992. See Ref. 29a, pp. 373–78
78. Deleted in proof
## CONTENTS

Jahn-Teller Phenomena in Solids, J. B. Goodenough ......................................................... 1
Isotropic Negative Thermal Expansion, Arthur W. Sleight ................................................. 29
Spin-Dependent Transport and Low-Field Magnetoresistance in Doped Manganites, J. Z. Sun, A. Gupta ......................................................... 45
High Dielectric Constant Thin Films for Dynamic Random Access Memories (DRAM), J. F. Scott ......................................................... 79
Imaging and Control of Domain Structures in Ferroelectric Thin Films via Scanning Force Microscopy, Alexei Gruverman, Orlando Auciello, Hiroshi Tokumoto ......................................................... 101
InGaN-Based Laser Diodes, Shuji Nakamura ......................................................... 125
Soft Lithography, Younan Xia, George M. Whitesides ....................................................... 153
Transient Diffusion of Beryllium and Silicon in Gallium Arsenide, Yaser M. Haddara, John C. Bravman ......................................................... 185
Semiconductor Wafer Bonding, U. Gösele, Q.-Y. Tong ................................................... 215
Cathodic Arc Deposition of Films, Ian G. Brown ......................................................... 243
The Material Bone: Structure--Mechanical Function Relations, S. Weiner, H. D. Wagner ......................................................... 271
Science and Technology of High-Temperature Superconducting Films, D. P. Norton ......................................................... 299

STUDIES OF MULTICOMPONENT OXIDE FILMS AND LAYERED HETERO STRUCTURE GROWTH PROCESSES VIA IN SITU, TIME-OF-FLIGHT ION SCATTERING AND DIRECT RECOIL SPECTROSCOPY, Orlando Auciello, Alan R. Krauss, Jaemo Im, J. Albert Schultz ......................................................... 375
Perovskite Thin Films for High-Frequency Capacitor Applications, D. Dimos, C. H. Mueller ......................................................... 397
RECENT DEVELOPMENTS IN CONDUCTOR PROCESSING OF HIGH IRREVERSIBILITY FIELD SUPERCONDUCTORS, J. L. MacManus-Driscoll ......................................................... 421
Point Defect Chemistry of Metal Oxide Heterostructures, Sanjeev Aggarwal, R. Ramesh ......................................................... 463
Processing Technologies for Ferroelectric Thin Films and Heterostructures, Orlando Auciello, Chris M. Foster, Rammamoorthy Ramesh ......................................................... 501
The Role of Metastable States in Polymer Phase Transitions: Concepts, Principles, and Experimental Observations, Stephen Z. D. Cheng, Andrew Keller ......................................................... 533
Processing and Characterization of Piezoelectric Materials and Integration into Microelectromechanical Systems, Dennis L. Polla, Lorraine F. Francis ......................................................... 563
Recent Advances in the Development of Processable High-Temperature Polymers, Michael A. Meador ......................................................... 599
High-Pressure Synthesis, Characterization, and Tuning of Solid State Materials, J. V. Bading ......................................................... 631