PZT thin film deposition techniques, properties and its application in ultrasonic MEMS sensors: a review

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Abstract: This paper describes an overview of the state of art in PbZr,Ti₁₋ₓO₃ (PZT) ferroelectric thin films and its applications in Micro Electro Mechanical Systems (MEMS). First, the deposition techniques and then the important properties of PZT films such as surface morphology, polarization and ferroelectric properties are reviewed. Two major deposition techniques such as sol-gel and Magnetron sputtering are given and compared for the film surface morphology and ferroelectric properties. Finally, the application of PZT thin film in MEMS ultrasonic sensors is discussed.

1. Introduction
Over the last 20 years, ferroelectric thin films found greater applications in the field of microelectromechanical systems (MEMS) and non-volatile memory. Piezoelectric thin films are widely used in MEMS application, because of their ability to generate large displacements, the higher sensitivity and higher energy densities with wide dynamic range and low power requirements.

PZT ceramics are of main importance in MEMS devices, predominantly in the field of sensors and actuators [1]. PZT thin film is often used as the actuating/sensing component in MEMS due to its excellent polarization values, dielectric constant, easy integration to various devices and piezoelectric constant. Also, PZT thin films show the extreme reduction of sintering temperature than bulk PZT ceramics. Devices that use PZT as active layer/component include micro-pumps and valves, ultrasonic sensors, thermal sensors, probes for medical imaging and nondestructive testing, accelerometers and for a new range of electronic components. Bottom-up and top-down are the two approaches of manufacturing technology used in the incorporation of ferroelectric materials with associated structural components and electronic circuitry. The bottom-up approach uses Spin coating/dip coating of a sol-gel precursor or Magnetron sputtering as deposition techniques for thin film deposition. Thin film compositions have significantly reduced processing temperatures (600-700 °C) where as the standard bulk ceramic have higher sintering temperature (1100-1400°C). A typical single layer thickness is around 0.1 micron and films are built up to the required thickness by successive deposition of several single layers. On the other hand top-down approach for micro-scale device fabrication is done by adhesive bonding. The layer thickness less than ~80 microns can be deposited using top-down approach.
In this work, the physical and chemical deposition techniques for PZT films and properties of PZT films such as surface morphology and ferroelectric properties (remanent polarization and coercive field) are reviewed. Two major deposition techniques such as sol-gel and Magnetron sputtering are discussed in detail and compared. Finally the applications of PZT thin films in micromachined ultrasonic transducers using MEMS technology are discussed.

2. Thin film deposition techniques and film properties

2.1. Thin film deposition techniques

The physical and chemical deposition methods have been investigated for the coating of PZT films. The physical methods include ion beam sputtering, magnetron sputtering [16, 17] and pulsed laser deposition (PLD) [2, 3]. Chemical deposition techniques consist of metal-organic chemical vapor deposition (MOCVD) and chemical solution deposition (CSD) [5, 6]. Conformal coating of three-dimensional objects is possible with MOCVD or CSD techniques. CSD is used in the sensor industry as it is a low cost technique for small-scale production. Since the films coated using CSD are initially amorphous in nature, to convert from amorphous to crystalline post-annealing treatments are needed. All the other physical methods described above allow in-situ growth. Although the CSD technique seems very diverse from the vacuum deposition techniques like sputtering or PLD, there are still some common features:

• The properties of the substrate strongly influence the crystallinity and texture of the film.
• The quality of the interface between substrate and film is dependent on the substrate chemistry, for example: reactivity of the substrate surface with the deposited phase constituents, diffusion coefficients etc. [4].
• Since the initial state is a disordered one, the lattice energy has to be brought to the system, either thermally or by a physical way.
• The growth is nucleation controlled [7].

Among these thin film deposition techniques, sol-gel and sputtering methods have been investigated mainly in recent years.

Sol-gel method: Sol-gel technique is most widely used method because of its ease of fabrication for PZT films and low cost. This method offers four unique advantages: 1) the stoichiometric chemical composition of PZT films can be easily controlled. Since the physical properties strongly depend on the defined control of the chemical composition stoichiometry control is for complex oxides such as PZT 2) sol-gel processing is inexpensive, due to its 100% usage of precursors. 3) Bulk production is possible using sol-gel process and it is compatible with device fabrication processes. 4) Using sol-gel method direct patterning of microstructures without using conventional etching is possible [7, 9-10]. Even though sol-gel method has several advantages, there are tremendous challenges to overcome. Before discussing these challenges, the sol-gel process for PZT thin films is explained below.

• Deposit bottom electrode on silicon substrate.
• Dip-coat or spin-coat PZT sol onto the silicon substrate. Lead acetate trihydrate, tetrabulyt titanate, and zirconium n-butoxide are used as precursors, and acetylacetone is the chelating agent; glycol methyl ether is the solvent.
• The PZT/silicon structure is sintered at high temperature of range from 600 °C to 700 °C to densify the PZT film and to form the desired perovskite crystalline structure. The sintering time will be 4 to 6 hours followed by the deposition of top electrodes, as shown in Figure 1.
Three main challenges in depositing PZT thin films using sol-gel are as follows:

1) Defects such as cracks and delamination are the main challenges. The presence of cracks short-circuit the top and bottom electrodes, also causes aging and fracture of PZT thin films. Delamination results in mismatch of thermal expansion coefficient (TEC) between the bottom electrode and the PZT film. Present research works are mainly for PZT films with thickness lesser than 1 μm [12-13]. Since, these PZT films consist of multiple coatings, with each coating thickness ranging from 15 nm to 100 nm. But the corresponding crack-free area is usually about 1 mm² [12,13]. Thus sol-gel based fabrication of crack-free PZT films with thickness ranging from 1 μm to 30 μm remains open thus far.

An innovative research is needed to develop crack-free PZT films in above thickness range.

2) Presently, metal (e.g., Pt/Ti) is used as electrodes. When sintering temperature is above 600 °C electrodes become thermally unstable. This results in porosity in the electrodes; as depicted in the dark regions in Figure 2. [14]. Presence of holes degrades the functions of electrodes because oxygen in the PZT films diffuses into the substrate resulting in dielectric loss [15]. Apart from this, TEC of metal electrodes is different from that of PZT. The mismatch of TEC results in cracks in the PZT films, particularly when the film thickness goes above 1 μm. Diffusion of oxide electrodes into the PZT films results in change in the chemical composition of PZT. As a result, reduction in the polarization performance and two undesired pyrochlore phases can appear in the PZT films [8].

3) The higher sintering temperature will significantly improve the piezoelectric properties of the films. When the sintering temperature is 650 °C, the grain size of PZT film is relatively small. For PZT crystalline particles, the piezoelectric effect reduces as the grain size decreases. Increase of the sintering temperature to 800 °C, for example, will increase the grain size and enhance the piezoelectric properties significantly. But it causes several adverse effects. First, chances of delamination of PZT films will be high, because higher sintering temperatures causes higher thermal stresses. Second, increase of sintering temperature will speed up the thermal instability of metal electrodes. Third, elevated sintering temperature will cause degradation of piezoelectricity due to the loss of PbO due to its volatility [15].

Figure 1. Sol-gel deposition method for PZT films

Figure 2. Thermodynamic instability of Pt/Ti electrodes, 750°C for 1 hour [14]
**Sputtering Method:** PZT ceramic target were prepared by stoichiometric ratio analytically pure ZrO2, TiO2 with excessive PbO because Pb volatalizes easily in sputtering and anealing. A target to be deposited is bombarded by energetic inert gas ions, such as argon, at pressure of 0.1–10 Pa. This causes the atomic species of the target material to be removed away from the surface of the target and deposited onto the surface of silicon substrates. The depositing layer will have the same chemical composition as that of the target. The materials for MEMS application that can be deposited using sputtering method include Al, Ti, Cr, Pt, Al/Si, Ti/W, amorphous silicon, glasses, and ceramics such as PZT and ZnO. Deposited films have fine grain size and uniform film thickness. But the type of stress developed and its magnitude in the sputter deposited films depend on process parameters such as the properties of the material to be deposited and the substrate, deposition rate, thickness and substrate temperature [16, 17].

2.2 **PZT thin film properties**

In this section the properties such as surface morphology, optical and ferroelectric properties of the deposited PZT films are discussed.

**AFM Studies:** Figure 3 shows the AFM images of PZT (Zr/Ti = 52/48) thin films deposited using sol-gel and sputtering methods. Mean roughness of films deposited using sol-gel and sputtering were found to be 10 nm [16] and 51.01 nm [9] respectively. The AFM images of PZT films shows that the films deposited using sol-gel method are hazy and clear cracks surface and no oriented growth, but the sputtered PZT films are well crystallized, crack free and has almost uniform grain distribution. The average surface roughness of PZT thin films deposited on Pt/Si (1 1 1) and Pt/Si (1 0 0) substrates by sol–gel method are reported as 0.7 nm and 3.832 nm respectively [11]. Hence it is proven that the smooth nanosized surface roughness films enhances the polarization.

**P-E Measurements:** Figure 4 shows the remanent polarization, \( P_r \), and coercive field, \( E_c \), of the PZT thin films deposited using sol-gel [11] \( (P_r = 56.8 \, \mu C/cm^2, \quad E_c = 50 \, kV/cm) \) and sputtering methods \( (P_r = 71.9 \, \mu C/cm^2, \quad E_c = 79.14 \, kV/cm) \) [17]. Table 1 shows the values of \( P_r \) and \( E_c \) of sol-gel PZT films are lower than that of sputtered PZT films. Since the Sputtered PZT films are crack free and well crystallized they exhibit higher remanent polarization. Also values of \( P_r \) and \( E_c \) reported as 17 mC/cm² and 50 kV/cm respectively [19]. The \( P_r \) and \( E_c \) values of 9 mC/cm² and 39 kV/cm respectively are reported, by [18]. The enhancement in the ferroelectric properties such as \( P_r \) in this study may be because of a larger grain size of about 1 mm compared to the films deposited by a XeCl excimer laser of wavelength 308 nm in which the maximum grain size of the films observed was 0.1 mm [21]. Higher \( P_r \) value of 30 mC/cm² was reported by [20]. A remnant polarization of 13 mC/cm² (for randomly oriented, hazy films) and 23 mC/ cm² (for well crystallized) was reported by [22].

![Figure 3](image-url)  
*Figure 3. AFM images of PZT thin films deposited using sol-gel [9] and sputtering method [16] respectively*
Table 1. Comparison of ferroelectric properties of PZT films deposited using sol-gel and sputtering methods.

| Properties                      | Sol-gel | Sputtering |
|---------------------------------|---------|------------|
| Remanent Polarization, \( P_r \) (\( \mu C/cm^2 \)) | 36.8    | 71.9       |
| coercive field, \( E_c \) (kV/cm)  | 50      | 79.14      |

Figure 4. Polarization – Electric field hysteresis loop for PZT thin films deposited using sol-gel [11] and sputtering method [17] respectively.

3. PZT thin film application in ultrasonic MEMS sensors

Presently, main research concentration is on micromachined ultrasonic transducers for sensor and actuator application. During 1990s the Stanford University fabricated the first ultrasonic piezoelectric transducers. From several decades, ultrasound (frequency from tens of kilohertz to hundreds of megahertz) has found great application in industrial and biomedical applications, ultrasonic actuation [27], ultrasonic sensing, medical imaging [28], therapeutic ultrasound [29], and particle and cell manipulation [30]. The methods used to excite ultrasound include the piezoelectric effect, magnetostriction, and the photoacoustic effect [9, 10]. Most common method used is the piezoelectric effect.

3.1. Micromachined ultrasonic transducers

Basic ultrasonic transducer module includes suspended piezoelectric membrane with high conducting top and bottom electrodes, usually Au or Pt. The cross section of an elemental piezoelectric ultrasonic transducer is shown in Figure 5(a). The resonant frequency of this structure is designed as 100 kHz. These conventional transducers were fabricated using Silicon On Insulator (SOI) wafer and piezoelectric PZT film was deposited by sol-gel method. For this type of conventional transducers, the anti-resonant frequency depends on the thickness of the piezoelectric layer [28]. Direct dependency of the resonant frequency on the PZT film thickness limits the geometry and structure of transducer for particular applications. This structure limits the energy transmission and bandwidth reduction because of impedance mismatch between piezoelectric layer and load. Hence great difficulty and complexity in manufacturing [26].

Figure 5. Typical structures of (a) piezoelectric ultrasonic transducers; (b) CMUTs and (c) \( d_{31} \)-mode PMUTs [24]
To overcome the problems associated with conventional transducers micromachined ultrasonic transducers (MUT) are fabricated using MEMS technology. The two types MUT include capacitive micromachined ultrasonic transducers (CMUTs) (Figure 5(b)) and piezoelectric micromachined ultrasonic transducers (PMUTs) (Figure 5(c)). Reference [28] compared these two MUTs for their electrical properties, radiation properties, and reported that CMUTs exhibit high bandwidth but a reduced pulse sensitivity.

A CMUT structure is a miniaturized capacitor that contains a thin suspended membrane (for e.g., silicon nitride) over a cavity over a silicon substrate as shown in Figure 5(b). When the CMUT is excited by the application of dc voltage between the two electrodes, there will be a deflection of the membrane, and due to electrostatic forces membrane get attracted towards the silicon substrate. This attraction of membrane towards the substrate is resisted by the stiffness of the membrane [32]. When ac voltage input is applied between electrodes, oscillations of the suspended membrane generate ultrasound. In PMUTs the piezoelectric effect of membrane produces lateral strain in the membrane which in turn causes the deflection of the piezoelectric membrane. Here, thickness of the piezoelectric film does not influence the resonant frequency of the PMUT. But the shape, dimensions, intrinsic stress and mechanical stiffness of membranes influences the resonant frequency of PMUTs [24]. PMUTs require a lesser voltage bias, fewer geometric and design constraints and allow easy integration with low voltage electronics compared to CMUTs. PMUTs have several other advantages, such as higher sensitivity, higher capacitance and lower electrical impedance than CMUTs. Use of piezoelectric thin films in the PMUT fabrication further provides large output signals, low loss and high signal-to-noise ratios (SNR) [25].

### 3.2. Materials for PMUTs

Figure 6 shows the schematic of the single PMUT. A PMUT element consists of piezoelectric layer sandwiched between two electrodes. The piezoelectric material includes PZT, ZnO, AlN, PVDF. Among this PZT is the most widely used material because of its high dielectric constant, excellent polarization, high energy density and large coupling co-efficient. To generate the ultrasound, PZT thin film is deposited on Pt/Ti/Si substrate. The two electrodes are made of Pt/Ti; one of these electrodes is at the top of the PZT layer and second is between PZT and silicon substrate, since the Pt has high thermal conductivity (~71.6 W/ (mK)) and good stability at high temperature [24-25].

To enhance the adhesion of the Pt to the Silicon substrate Ti is introduced. Also Ti improves the formation of perovskite structure of PZT films and Silicon oxide (SiOₓ) layer acts as passivation layer. Silicon substrates/wafers used for MEMS devices can be single crystalline, polycrystalline (polysilicon). The type of application and manufacturing process are the factors that decide the type of the silicon substrate to be used for PMUTs [23, 28]. For MEMS application commonly used single crystal silicon wafers are having 100 mm and 150 mm diameter, 525 – 650 mm thickness and single-side polished. Common crystal orientation of wafers are (1 0 0) and (1 1 1) (100) and (111) with n or p type dopant. The required mechanical, electrical properties of the silicon wafer and silicon oxide are given in Table 2. Table 3 gives the thermal and physical properties of the silicon and silicon oxide [1, 2].
Table 2. Mechanical and electrical properties of silicon wafer and silicon oxide

| Material     | Young’s modulus (GPa) | Relative Permittivity | Band gap (eV) | Dielectric Strength (V/cm x 10^6) |
|--------------|------------------------|-----------------------|---------------|-----------------------------------|
| Silicon      | 160                    | 11.7                  | 1.12          | 0.3                               |
| Silicon oxide| 73                     | 3.9                   | 8.9           | 5-10                              |

Table 3. Thermal and physical properties of silicon wafer and silicon oxide

| Material     | TEC 10^6 / °C | Thermal Conductivity (W/mK) | Density g / cm^3 | Melting/sublimation point (°C) |
|--------------|---------------|-----------------------------|------------------|-------------------------------|
| Silicon      | 2.6           | 157                         | 2.4              | 1415                          |
| Silicon oxide| 0.55          | 1.4                         | 2.2              | 1700                          |

4. Conclusions
The state of art in PbZr₀.₅Ti₀.₅O₃ (PZT) ferroelectric thin films and the deposition techniques such as physical and chemical vapor deposition techniques for PZT thin films are reviewed. Two major deposition techniques such as sol-gel and magnetron sputtering are given and compared for the film surface morphology and ferroelectric properties such as remanant polarization, coercive field. The application of PZT thin films in machined ultrasonic transducers is discussed. Comparison between conventional transducers and the micro machined ultrasonic transducers are made. The materials used in piezoelectric micromachined ultrasonic sensors are discussed.

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