Ferroelectric films for MEMS type devices using novel hybrid processing technology

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Ferroelectric Films for MEMS Type Devices Using Novel Hybrid Processing Technology

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School of Electrical & Electronic Engineering

A thesis submitted to the Nanyang Technological University
in fulfillment of the requirement for the degree of
Doctor of Philosophy

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SUMMARY

SUMMARY

Lead zirconate titanate (PZT) films are promising for MEMS type micro-devices applications because of their extremely high electromechanical coupling coefficients and excellent piezoelectric response. PZT piezoelectric film integrated on silicon substrate has been the subject of considerable attention in recent years. This thesis has presented a broad range of work, which aimed at developing, characterizing and evaluating PZT ferroelectric thick films for MEMS type device applications that could be integrated with silicon micromachining.

A novel hybrid technique based on nano-sized powders and homogenous matrix of sol-gel precursor composite has been developed. It is a simple and inexpensive method for fabricating composite thick films and bulk ceramics at low processing temperature. With this novel processing approach, high density of green bodies can be achieved; agglomeration between particles can be eliminated; low crystallization temperature can be realized; and sintering temperature to get fully dense materials can be remarkably reduced.

Dense materials both in films and bulk ceramics have been fabricated at low processing temperature using this novel hybrid sol-gel composite technique. Screen-printed PZT thick films on Au/Al₂O₃ and bulk ceramics, with sub-micron grains, could be produced with the sintering temperature remarkably decreased from 1100°C to 800°C. The sintered bulk ceramics have a relative density as high as 95.5%. The dielectric and ferroelectric properties of the PZT ceramics are in close agreement with the widely reported results.

SUMMARY

The novel technique has been refined and developed for the specific application of MEMS type devices. By suspending PZT powder in PZT xerogel solution, uniform and stable slurry was made that can be used to deposit PZT composite thick films on Pt/Si substrate. The resultant crack-free films after annealing have dense and uniform microstructures. The grains in the films developed fully and have an average size of 30 nm. Dielectric and ferroelectric properties have been investigated.

Optimization of the hybrid sol-gel composite process for thick film deposition has been realized by isolating and controlling the individual parameters of slurry characteristics and coating process. Slurry characteristics, including solution concentration, powder size, powder-solution ratio and vehicle content, have prominent effects on microstructure and electrical properties of the films. High temperature heat treatment could improve the electrical properties by increasing the grain size and crystallinity of the films. Replacing Ti by TiO_2 as an adhesion layer between platinum and underlying layers is an effective approach to prevent the peeling under high temperature annealing. Alternating the loaded powder with submicron sized or pre-heat treated at high temperature could produce larger grain size in films or increase the degree of crystallinity of the powder, and thus improve the electrical properties. Back filling with pure xerogel solution and application of cold isostatic pressing technique could also improve the microstructure and electrical properties of thick PZT composite films.

This thesis has also presented a new combination of silicon micromachining technique and thick PZT film to produce piezoelectric microtransducers for ultrasonic application. Thick piezoelectric PZT composite films were deposited on Pt/Ti/LTO/ Si_3N_4 / SiO_2 /Si substrates. Square diaphragms ranging from 0.5 mm to 2

SUMMARY

mm in dimension were successfully fabricated. Phase transducer arrays with 2 to 5 rings have been realized. Deflection amplitude, frequency response, and acoustic transmitting properties were investigated. The processes developed in this research are beneficial for future research on PZT-based MEMS type devices.

CHAPTER 1 INTRODUCTION

1.1 Motivation

Micro-electro-mechanical systems, or MEMS, include both sensors and actuators that are fabricated on silicon together with control circuits and other electronic devices. It has become an important area of technology, building on the success of the microelectronics industry over the past 50 years. A number of excellent review articles on the progress in the MEMS field have recently been published [84, 85]. Three general themes are commonly exploited in MEMS: miniaturization, multifunction, and microelectronics. MEMS have a wide range of applications including automotive, electronics, biomedical, and information processing [1, 2]. These devices generally use silicon micromachining technologies and can be directly integrated with on-chip electronics. Silicon micromachining, taking advantage of well-established processes and materials in microelectronics, is commonly used to fabricate mechanical microstructures. As a result, in the early work, the materials used in MEMS area were limited to those used in microelectronics. With the development of research, numerous MEMS devices with sensors, actuators, and micro-optical components have been demonstrated based on a wide variety of physical operating principles.

Piezoelectric MEMS has been usually operated in one of two modes: sensor or actuator. When used as a sensor one usually detects a change in internal dipole moment within the piezoelectric crystal induced through either a stress or the change of relate environment. This change in internal dipole moment is usually detected in the form of a charge or voltage developed across a set of appropriately located

electrodes surrounding the piezoelectric crystal. When used as an actuator, a voltage is applied across a set of electrodes, thereby inducing a strain or deformation of the crystal. This controlled deformation is used to do actuation.

There is a strong interest in introducing ferroelectric lead zirconate titanate (PZT) materials for MEMS type devices [3-6]. They are particularly attractive because they can be incorporated into actuator and sensor structure in a wide variety of configurations and can be operated by using either direct charge detection or wave/resonance type phenomena. Ferroelectric materials offer the possibility of enhanced performance in these applications due to the extremely high electromechanical coupling coefficients. The large piezoelectric effect in the ferroelectric material lead zirconate titanate $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$, or PZT, is very important for both physical force sensing and micro-electro-mechanical actuation. PZT ceramics, in their paraelectric and ferroelectric states, have been used extensively in many applications such as multilayer capacitors, actuators, ultrasonic motors, and infrared sensors because of their superior piezoelectric and pyroelectric properties. Since 1984, ferroelectric materials have been widely investigated for microelectronic applications in film devices, including applications in memories, microelectromechanical systems (MEMS) and ultrasonic imaging. Potential applications include membrane sensors, micro-accelerometers and micro-motors. In general, these devices are based on films of thickness less than 1 μm .

High quality, crack free and homogeneous PZT thin films with thickness less than 1 μm have been prepared by various methods including RF sputtering [7], laser ablation [8], metallo-organic decomposition [9] and sol-gel process [10]. However, thin film actuators cannot provide enough generative force for relative large actuation, and other devices in MEMS application. For many sensor/actuator applications, PZT

films should be comparatively thick ($>1\text{ }\mu\text{m}$) because the piezoelectric response increase with increasing film thickness. An increase in thickness reduces the strength of the electric field produced within the film by the applied voltage. Hence a large voltage can be applied before the film reaches its breakdown field (typically $= 1\text{ MV/cm}$). This allows for the large displacements necessary for electromechanical coupling devices. To achieve high performance MEMS devices, it is necessary to produce dense PZT piezoelectric films with thickness ranging from 1 to $50\text{ }\mu\text{m}$ on silicon wafer for the purpose of producing large piezoelectric displacement and generative force. However, depositing and processing of these thick films presents significant challenges. Even lapping or sawing bulk ceramics to a thickness less than $50\text{ }\mu\text{m}$ is very difficult under any circumstance. PVD and CVD of oxide films have often been regarded too expensive, slow and difficult. Thus, deposition of thick piezoelectric films on silicon wafer for potential application in MEMS is becoming an attractive topic in recent years.

At present, thick films with thickness of tens of micron can be obtained by the screen-printing and tape casting techniques. However, the PZT thick films deposited by these methods have low density; and the high sintering temperature is not compatible with silicon micro-machining process. Accordingly, a low-temperature based on conventional sol-gel process technique has been developed. Generally, the limited thickness of a crack-free single layer film is $0.3\text{ }\mu\text{m}$ for sol-gel process technique. Although repeated coating and drying permit the buildup of thicker films, $1\text{ }\mu\text{m}$ is the general limitation above which film will have cracks or peel off from the substrate, and the fabrication is time-consuming. Barrow *et al.* have reported the thick PZT ceramic coating using a sol-gel based ceramic-ceramic 0-3 composites [65, 104]. Chen *et al.* prepared the PZT thick films using titanium diisopropoxide

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biacetylacetone as raw material [33]. However, preparing thick uniform PZT films with large area by the sol-gel technique is still challenging, due to cracking caused by the large stress between the substrate and film.

The cracking of PZT films has two main deleterious effects - introduction of possible paths for electrical shorts, and lowering of piezoelectric properties. For example, intergranular cracking lowers d_{31} reducing intergranular connectivity.

Laterally expanding grains create macroscopic lateral strain by “pushing against” one another. When intergranular connectivity is lost, the macroscopic lateral strain is greatly reduced, resulting in a lowered macroscopic value of d_{31} . Therefore, it is necessary to develop a new process for fabricating dense, crack-free PZT thick films on silicon substrates at relative low process temperatures so as to fill up the gap between thin film deposition and thick film processing. It will have a significant scientific and technological impact.

While PZT thick film deposition is a complex research area, integration of piezoelectric PZT layer into MEMS devices poses another more serious challenge. The process of incorporating an active piezoelectric layer between two electrode layers on top of a structural layer introduces several materials related problems. Among these are the interaction between the PZT layer and the electrodes, and the effect that these interactions have on the piezoelectric properties and adhesion of the two dissimilar materials: Pt bottom electrode layer and PZT piezoelectric layer.

7.7 Objective

In this thesis, the ultimate goal is to approach the fabrication and application of ferroelectric PZT composite thick films for MEMS type devices. Lead zirconate titanate (PZT) ferroelectric thick films, with a composition at morphotropic phase boundary (MPB) of $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ is deposited with a thickness of tens of micron

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to produce the required displacement or driving force. A sol-gel based novel hybrid processing technology is developed to coat the PZT composite films on platinum coated silicon substrate by spin coating. The careful and systematic investigations focus on the optimization of the novel hybrid processing technology and its integration with silicon micromachining technologies for MEMS type devices applications. Problems in this work will be studied in order to make high-performance, miniature, mass-production-compatible, and potentially circuitry-integratable MEMS type devices.

1.2 Major contributions

The major contributions achieved in this study are summarized as follows:

1. The novel hybrid processing technology has been successfully developed by combining high-energy ball milling process and sol-gel method. PZT powders with fine size have been uniformly dispersed into PZT xerogel solution with the aid of vehicle.
2. The low temperature processing character of the novel hybrid technique has been realized with the loading of nano-sized PZT powder into xerogel solution matrix and validated through the sintering investigation of screen-printed PZT thick films and bulk ceramics.
3. Crack-free and uniform PZT composite thick films on platinum coated silicon substrate have been coated using slurries produced by the novel hybrid processing technology.
4. Optimization of the novel hybrid processing technology has been realized in terms of the microstructure, dielectric and ferroelectric properties of the coated PZT composite thick films.

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5. Integration of PZT composite piezoelectric films on silicon wafer with micromachining technologies has been investigated. The actuation properties, including deflection amplitude, frequency response and acoustic transmitting characteristics of piezoelectric micro-ultrasonic transducer diaphragms with different dimensions have been investigated as well.
6. A phased ultrasonic array for loudspeaker in audio beam application has been successfully designed and fabricated.

1.3 Organization of the thesis

This thesis emphasizes on the development of PZT composite thick films on platinum coated silicon substrate for MEMS type devices application using the novel hybrid processing technology. It comprises of seven chapters.

Chapter 1 provides a general introduction on the fabrication and application of PZT thick films.

In Chapter 2, the ferroelectric PZT system, deposition of ferroelectric films, sol-gel processing technology, and application of piezoelectric films to MEMS type piezoelectric devices are introduced as the background.

Chapter 3 is devoted to the high-energy ball milling technique and the primary experimental procedures to fabricate the PZT precursors using the hybrid processing technology. The relative microstructure and electrical characterizations are provided.

Chapter 4 describes the development of the novel hybrid processing technology. Its applications to screen-printed PZT thick films on alumina substrate and bulk ceramics are presented in terms of the sintering experiments. Merits of the hybrid route with low processing temperature are discussed.

In Chapter 5, this novel processing technology is further exploited to deposit PZT composite thick films on platinum coated silicon substrate. Optimization of the

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hybrid processing technology, which includes slurry characteristics, annealing, PZT powder loaded, application of back filling and CIP technique, is realized in terms of microstructure, dielectric and ferroelectric properties, and I - V characterizations.

Chapter 6 devotes the integration of piezoelectric PZT thick films with silicon micromachining techniques for MEMS type piezoelectric devices fabrication. The design, process development and characteristics of square piezoelectric micro-ultrasonic transducer diaphragms are presented. The actuation properties, including deflection amplitude, frequency response and acoustic transmitting characteristic are investigated for diaphragms with different dimensions. A phase ultrasonic array used as loudspeaker in audio beam application is designed and fabricated.

Finally, the conclusion and recommendations for future work are presented in Chapter 7.

CHAPTER 2 BACKGROUND

The issues in this Chapter are important to understand the materials background and the experimental details presented in this thesis. Section 1 presents brief overview of the ferroelectrics and lead zirconate titanate (PZT) systems. Different approaches to deposit PZT ferroelectric films are reviewed in Section 2. Section 3 describes the sol-gel processing technology with view to deposit crack-free PZT thick films on platinum coated silicon substrate. Finally, applications of piezoelectric PZT thick films on silicon substrate for MEMS type devices are discussed in Section 4.

2.1 Ferroelectrics and lead zirconate titanate (PZT) systems

2.1.1 Ferroelectric materials

Ferroelectric materials can be defined as those which exhibit an equilibrium spontaneous polarization whose orientation can be reversed by an applied electric field. There are literally hundreds of materials known to be ferroelectrics. However, a group of ferroelectrics known as the “perovskite family” are perhaps the most extensively studied and technologically important. Ferroelectrics such as $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$, $(\text{Ba}, \text{Sr})\text{TiO}_3$, and LiNbO_3 belong to this family and have the general formula ABO_3 .

All ferroelectric materials are piezoelectric since they all have polar structures. At high temperatures, many ferroelectric materials do not have a spontaneous polarization since they have a higher symmetry crystal structure (the paraelectric phase). The transition point is defined as the Curie temperature (T_c). At temperature

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below T_c , a phase transformation occurs where the material distorts into a lower symmetric structure resulting in a ferroelectric phase with a spontaneous polarization.

Another important characteristic of ferroelectric is the polarization – electric field (P-E) hysteresis loop. This loop is the evidence showing that the spontaneous polarization can be reoriented along certain crystallographic orientations. The hysteresis in the P-E relation results from the stability of the polarization along the preferred crystallographic orientations and its resistance to reorientation. From the P-E hysteresis loop (see Figure 2- 1), several distinctive characteristics can be described. The saturation polarization (P_s), defined as an extrapolated value from the high field linear portion, refers to the total polarization attributable to the reversal of the spontaneous polarization. The remnant polarization (P_r) refers to the amount of polarization remaining after removal of applied electric field. This reflects the degree of alignment of the dipole moments in a given ferroelectric. In an ideal single crystal, the hysteresis loop would have a rectangular central region with $P_r = P_s$. The coercive field (E_c) refers to the field value required to reverse the direction of the polarization. Real hysteresis loops, especially in polycrystalline materials, are often slanted – different regions in the material reorient at different fields.

At equilibrium, ferroelectric crystals form domain structures so that there is no net polarization. Additionally, polycrystalline ferroelectrics have randomly oriented grains (each containing its own set of domains), which further act to cancel out all internal polarization so that the bulk sample has no net polarization. In order for a bulk ferroelectric to be macroscopically pyroelectric or piezoelectric, dipoles must be reoriented and aligned by application of a steady electrical field in excess of the coercive field. This process is termed as “poling”. In a piezoelectric application,

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actuation is then done with a very small electric field (in comparison with the coercive field) so as not to depolarize the sample.

Figure 2-1. Schematic of polarization hysteresis for a ferroelectric.

2.1.2 Ferroelectric PZT systems

One of the most extensively studied ferroelectric compositional families is the lead zirconate titanate system. Lead zirconate titanate [$\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ or PZT] is the solid solution of antiferroelectric lead zirconate (PbZrO_3) and ferroelectric lead titanate (PbTiO_3). In general, the term PZT refers to a wide range of compositions with the chemical formula $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ rather than a single compound.

The crystal structure and properties of PZT strongly depend upon the Ti/Zr ratio. The phase diagram for the PZT system is shown in Figure 2-2. The crystal structure of PZT above the Curie temperature (T_c) is paraelectric phase ($m3m$) with a

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cubic perovskite structure, where the B site atoms (Zr or Ti) are located at the center of the unit cell. It should be noted that the Curie temperature varies from 230°C to 490°C depending on the Zr/Ti ratio. After cooling below the Curie temperature, PZT undergoes the phase transition from a paraelectric phase to a ferroelectric phase. The crystal structure of the ferroelectric phase is determined by the Zr/Ti ratio. Compositions from $\text{Pb}(\text{Zr}_{0.93}\text{Ti}_{0.07})\text{O}_3$ to $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ are rhombohedrally distorted perovskite ($3m$), and compositions from $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ to PbTiO_3 are tetragonally distorted perovskite ($4mm$). Compositions in excess of ~93% Zr assume an orthorhombic, antiferroelectric structure and are not piezoelectric.

Figure 2-2. Phase diagram of the PbZrO_3 - PbTiO_3 (PZT) system.

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One of the interesting features in the PZT systems is a morphotropic phase boundary (MPB) in which rhombohedral and tetragonal phases co-exist at the approximate composition 53% PbZrO_3 , 47% PbTiO_3 . It is placed at the point where the rhombohedral and tetragonal phases are co-present. The existence of an MPB may be related to the instability of one ferroelectric phase against another upon a critical composition change. It has been experimentally observed that the maximum values of the dielectric constant and the piezoelectric coefficients of PZT ceramics at room temperature occur on this boundary. In addition, the maximum value of the remnant polarization is also observed near MPB ($\text{Zr/Ti} = 56/44$). It is suggested that the availability of eight possible directions of ferroelectric polarization in the rhombohedral phase along with six in the tetragonal phase in the phase coexistence region around MPB can substantially enhance the alignment of otherwise randomly oriented ferroelectric domains on the application of a strong dc poling field. In other words, the coexistence of the two phases allows 14 permissible polarization orientation states and therefore easy switching leads to the well known fact that near MPB, bulk form PZT exhibits maxima for both dielectric constant ϵ_r and remnant polarization P_r . The solid solution phase diagram of PZT system for thin films, however, differs slightly from the bulk due to epitaxy-induced strains and interfacial defect formation. Similar experimental results have been reported in other binary piezoelectric ceramic systems, such as the PbTiO_3 - PbSnO_3 and the PbTiO_3 - PbHfO_3 system.

Recent investigations regarding the structure of PZT near MPB suggest that the phase diagram of PZT is more complex than previously thought [11-13]. For example, synchrotron x-ray powder diffraction study by Noheda *et al.* have revealed the existence of an unexpected low temperature monoclinic phase of PZT at the MPB

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composition, which provides the bridge between the tetragonal and rhombohedral phases and facilitates polarization rotation. Furthermore, it has been suggested that the local (microscopic) structure of a PZT near MPB differs strongly from its average (macroscopic structure). Although the origin of physical and electrical phenomena near MPB is still not completely clear, current literature says that the maximum piezoelectric response near MPB is clearly expected for both PZT ceramics and single crystal based on the experimental observation and theoretical calculation [87].

2.1.3 Effects of composition on piezoelectric properties of PZT

Though the maximum piezoelectric effect was found in the composition of PZT at the MPB of Zr/Ti=53/47, in practice, PZT ceramics are often modified to meet the stringent requirements for various applications. For example, for materials used as underwater sound projector, a high Q_m and a small dielectric loss ($\tan\delta$) under high fields are desirable, while for materials used for electro-acoustic transformers, a high electromechanical coupling coefficient (K_p) and a high relative permittivity (ϵ_r) are required. Basically, three types of additives have been employed in the compositional modification of PZT. These typical additives and their effects on the piezoelectric properties of PZT are summarized in

Table 2-1 [86].

It has been confirmed [14] that the undoped PZT ceramics possess p-type conductivity (hole-type semiconductor) due to the lead oxide evaporation from the PZT sample during the sintering process, which creates Pb vacancies in the sintered PZT ceramic. Therefore, space charges, i.e., negative charges and hole-carriers, increase dramatically in a PZT ceramic with hard doping ions. It will cause an internal field E , inside the grains of PZT, and this field E_s may inhibit domain motion. The

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inhibition of domain motion reduces the dielectric loss (including the energy loss in domain vibration hysteresis), and therefore Q_m is enhanced.

Table 2-1. Typical additives to PZT and their major effects on piezoelectric properties.

Additives	Major effects
Isovalent additives: Ba ² or Sr ² for Pb ² Sn ⁴ for Zr ⁴ or Ti ⁴	Lower curie point Higher permittivity
Soft dopants: La ³ , Nd ³ , Sb ³ , Bi ³ or Th ⁴ for Pb ² Nb ⁵ , Ta ⁵ , Sb ⁵ or W ⁶ for Ti ⁴ or Zr ⁴	Higher permittivity/dielectric loss Square hysteresis loops, low Ec Greatly increased electrical resistivity Higher K_p Much lower Q_m
Hard dopants: K or Na for Pb ² Fe ³ , Al ³ , Sc ³ , In ³ or Cr ³ for Ti ⁴ or Zr ⁴	Lower permittivity/dielectric loss High Ec, more difficult poling and depoling Moderately lowered electrical resistivity Lower K_p Much higher Q_m

2.1.4 Effects of microstructure on piezoelectric properties of PZT

The microstructure of ceramics includes factor such as grain size and/or grain boundaries, density and/or porosity and homogeneity.

The grain size of PZT ceramics depends on the compositions and sintering conditions. In general, the grain size of PZT ceramics increase with increasing sintering temperatures and sintering time, from submicron to about 10 μm . Metal oxide dopants affect the grain growth during sintering process. Consequently, the effect of the grain size on the piezoelectric properties strongly depends on the

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compositions and sintering conditions. The deterioration of the piezoelectric properties with decreasing grain size is probably related to fewer domains and less mobile domain walls [15]. It is also reported that below a critical size, the formation of ferroelectric domains is not energetically favorable [16].

The density and/or porosity that affect the piezoelectric properties are dependent on the sintering conditions. Sintering in oxygen atmosphere is reported to facilitate the pore-elimination process [17]. The PZT ceramics possess higher density and the grain growth is suppressed with the increase of oxygen partial pressure. Thus the K_p is improved in comparison with that sintered in air.

Homogeneity is found to have a more profound effect on the piezoelectric properties. It is well accepted that inhomogeneity in the PZT ceramics in which the properties, such as ϵ_r and K_p , are very dependent on the Zr/Ti ratio near the MPB [18]. Also the piezoelectric properties for the latter materials sintered at 1000°C are inferior to those sintered at 1200°C, though having similar densities and grain sizes. The lower values are believed to be related to the crystallinity of materials being less developed. The associated defects thus result in stiffening out of the extrinsic polarizability (domain wall motion) [19].

2.1.5 Special issues of piezoelectric properties of PZT films

As known from bulk ceramics, the piezoelectric and ferroelectric properties vary substantially with the compositional parameter. In case of bulk PZT ceramics, the maximum values of piezoelectric coefficients, dielectric constant, and polarization have been achieved at the morphotropic composition [20]. The large number of possible polarization directions and large extrinsic contribution at this boundary attribute to the superior properties. Therefore, the electromechanical properties of

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MPB bulk PZT are often used in designing MEMS devices; and many researches for PZT thin films have been focused on this composition. In addition, the piezoelectric coefficients of PZT thin films have been measured to be much smaller than those of bulk PZT at the same composition. It has been proposed that the reduced piezoelectric effect in thin films can be attributed to the clamping effect of the substrate and limited extrinsic contribution compared to bulk ceramics [21-24].

Trolier-McKinstry *et al.* have demonstrated that 1 μm is the critical thickness where piezoelectric response of PZT thin films is significantly reduced due to substrate clamping and thereby limited non-180° domain wall motion [22]. However, this critical thickness needs to be specified because physical and electrical properties of PZT films are strongly dependent upon composition (crystal structure), orientation, substrate types, and microstructure (grain size). Therefore, a quantitative evaluation regarding each material's parameter is required to confirm this in the case.

Although the bulk PZT ceramics have been relatively well investigated, there is still a lack of experimental reports for understanding on the piezoelectric properties of PZT thin films. Furthermore, deficient data with respect to single crystal or epitaxial films make it difficult to fully understand the mechanism of PZT materials.

With respect to compositional effect on the piezoelectric properties, Chen *et al.* [25] and Teowee *et al.* [26] observed the maximum piezoelectric coefficients near MPB composition of PZT films. However, Hibous *et al.* observed maximum values of piezoelectric coefficient in tetragonal composition [24]. Due to limited number of previous reports as well as inconsistency in microstructure, orientation, thickness and process in the literature, simultaneous assessment of results does not lead to a consistent conclusion regarding the importance of MPB. Furthermore, orientation dependence of polycrystalline PZT films on the piezoelectric coefficients is rarely

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reported due to difficulty in isolation of texture effect [27]. With respect to thickness effect, results showed the increased piezoelectric coefficient with increasing film thickness [23, 28]. Xu F. *et al.* tried to evaluate piezoelectric response quantitatively as a function of film thickness with a consideration of microstructure [23].

2.2 Ferroelectric thin film deposition methods

The deposition methods for obtaining films of PZT vary greatly, and include: sol-gel methods, pulsed laser ablation, evaporation, sputter deposition, ion beam sputtering, chemical vapor deposition, and screen-printing, etc. Of these methods, sol-gel method, which will be discussed particularly in next section, is perhaps the most explored and widely used method in research, while sputter and CVD deposition are preferred by industry because of its potential for mass production [29]. Screen-printing method is one of the well-established thick film deposition technologies both in research and industry.

2.2.1 Thin film deposition methods

To date, the most widely used deposition technique employed to synthesize ferroelectric thin films can be divided into two major categories: dry and wet processes (see Table 2-2). The dry process includes physical vapor deposition (PVD) and chemical vapor deposition (CVD). The wet process includes chemical solvent deposition (CSD) and chemical melt deposition (CMD). In each case, the objective is to provide an appropriate flux of atoms onto a substrate so that the required compound grows controllably on the surface. The source may be a bulk material of composition similar to that desired in the film, or solution or vapor streams containing the required atoms with the reaction forming the compound occurring at the substrate itself [30].

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2.2.1.1 Dry process

Generally, the PVD technique requires a high vacuum, usually better than 10^{-5} torr, in order to obtain a sufficient flux of atoms or ions capable of depositing onto a substrate. The advantages of the PVD techniques are: (1) high purity and cleanness, (2) compatibility with semiconductor integrated circuit processing, and (3) epitaxy/single crystal film growth is possible. However, these are offset by disadvantages such as (1) slow deposition rates, (2) difficult stoichiometry control in multi-component systems where evaporation or sputtering rates differ considerably, (3) high temperature post deposition anneal is often required for crystallization, and (4) high capital equipment acquisition and maintenance costs are required.

Sputtering and evaporation are examples of well-established and successful PVD techniques. Ion-beam assisted evaporation and sputtering are continuing to become more popular in order to increase film uniformity and deposition rates. Pulsed laser ablation, a technique which is similar in concept to low energy thermal evaporation, seems to be more advantageous. For example, it allows congruent transfer of target material, with high deposition rate and low processing temperature.

The CVD techniques are usually characterized by (1) high deposition rates, (2) good stoichiometry control, (3) large area, pin-hole free films, and (4) low initial equipment costs. However, the limited availability and toxicity of some of the precursors for the ferroelectric compositions have posed a real problem for this method.

2.2.1.2 Wet process

Combining the advantages of excellent composition control, spin-coat/spray-on/dip-coating capability, low deposition/pyrolysis temperatures and very low equipment costs, the wet chemical techniques, e.g. sol-gel and metal-organic

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decomposition (MOD), have already been quite successful and considered to be the most promising techniques for producing ferroelectric thin films. The sol-gel method involves the preparation of a sol with polymerisable oligomer species that polymerize during spin- or dip- coating deposition. The formation of such networks can be very important for microstructure and crystalline phase development when the films are heat-treated to obtain the crystalline ceramics. The MOD method is a similar technique as sol-gel. It involves the synthesis of a solution containing high molecular weight precursors such as carboxylates, which are deposited onto the substrate for further heat treatment causing densification and crystallization. The difference is that the solution does not form complexes or networks.

The common limitations for the wet chemical techniques are, for example, that film cracking occurs during the drying/firing process because that the loss of volatile organic tends to lead to a large volume shrinkage of the film; and further heat treatment is normally required to obtain desired crystal structure.

Table 2-2. Ferroelectric thin films deposition methods.

Dry process	Wet process
Physical Vapor Deposition (PVD) <ul style="list-style-type: none">• Sputtering• Evaporation: E-beam• Molecular beam epitaxy• Pulsed laser ablation	Chemical Solvent Deposition (CSD) <ul style="list-style-type: none">• Sol-gel• MOD (metal-organic deposition)• Electrochemical reaction• Hydrothermal growth
Chemical Vapor Deposition (CVD) <ul style="list-style-type: none">• MOCVD (metal-organic CVD)• PECVD (plasma enhanced CVD)• LPCVD (low pressure CVD)	Chemical Melt Deposition (CMD) <ul style="list-style-type: none">• LPE (liquid phase epitaxy)

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2.2.2 Screen printing method

Some researchers have investigated the formation of thick films of PZT using a screen printing process derived from bulk processing methods [31, 32]. These methods utilize commercially available PZT powders mixed with lead borosilicate (to facilitate binding during annealing) in an organic vehicle. These mixtures are roll-milled to achieve adequate mixing, and the resulting paste is screen printed through a stainless steel wire mesh to pattern a thick film (multiple applications can be used to produce thicker films). The resulting film must then be annealed at elevated temperature (1000–1200°C) in air to sinter the powders. The thick films produced by this method are desirable for microelectromechanical systems (MEMS) because of their potential to produce large actuation forces.

2.3 Sol-gel processing technology

The sol-gel processing route has found increasing applications in the production of high-quality powders, fibers, and films. The sol-gel process of PZT thin films has attracted great attention because of its (1) simplicity, (2) low processing temperature, (3) chemical homogeneity, and stoichiometry control, and (4) ability to produce uniform film over large areas. The crystallization and the texture development of sol-gel PZT thin films as a function of pyrolysis and crystallization temperatures have been extensively investigated [34,35, 85].

2.3.1 Some basic concepts

Commonly the term "sol-gel" is used to describe the chemical process in which polymeric gels are formed from metal-organic starting solutions. However, the use of this term is not consistent in the literature. In a narrower sense, a "sol" is a fluid, colloidal dispersion of solid particles in a liquid phase where the particles are

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sufficiently small to remain suspended by the Brownian motion. A "gel" consists at least two phases wherein a solid phase forms a network that entraps and immobilizes a liquid phase [36]. In a wider sense, this term is more broadly applied in the literature so as to include systems that are neither true sols nor true gels.

A basic step of the sol-gel technique for device applications is to coat onto a substrate with a polymeric precursor solution containing the requisite metal components in the required proportions, which then, because of solvent evaporation and/or continuing chemical reactions, transforms to a gel layer. The organic components of the gel are then eliminated by various heat treatments to form the desired crystalline ceramic film [37, 38].

2.3.1.1 Sol-gel chemistry

The most commonly studied sol-gel systems are based on the chemistry of metal alkoxide, $M(OR)_n$. Many of these species readily undergo hydrolysis and condensation reactions, leading to oligomer formation and eventual gelation [39, 40]. The key steps in the gel-forming reactions can be summarized as follows:

Hydrolysis:

Condensation:

Molecular weight and viscosity measurements have been proved useful in the study of the molecular complexity of both single and mixed alkoxides. The results have confirmed the formation of condensed polymeric alkoxy species. However, the precise atomic structure of partially hydrolyzed polymeric units making up the framework of the gels used in sol-gel processes is still not fully understood. Ideally

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the condensed species contained sol-gel precursor solutions should have an alternating arrangement of the constituent cations, and this chemical homogeneity should be retained through to the final ceramic. For thin film work the gel-forming solutions are coated onto suitable substrates by spin, dip, or spray coating techniques, after which drying and firing steps convert the coated gel into an oxide film. Among them, the spin-coating process is a popular and well adopted method for applying uniform coatings onto flat substrates.

2.3.1.2 Some features of sol-gel processing

Much of the driving force for the development of sol-gel processes for thin film production has stemmed from the promise of composition control and uniformity. This is advantageous since standard methods of film deposition such as sputtering or chemical vapor deposition (CVD) often lead to difficulties in controlling the stoichiometry of multi-component oxide films. Problems may arise from differences in the sputtering rates of the constituents or differences in vapor pressures of CVD precursor reagents.

In sol-gel processes, although chemical composition may be under good control, at its present level of development the sol-gel method for titanate films is severely limited by inadequate control of the drying and shrinkage stresses, which accompany the conversion of gel into an oxide film. During shrinkage the constraint of the substrate imposes tension in the plane of film, and the magnitude of the resultant stress increases with increasing layer thickness until a limiting thickness is reached beyond which the film cracks. Film cracking and the limit that places on layer thickness are major obstacles to the utilization of sol-gel routes as a practical means of producing films with the thickness required for many device applications, such as micro-actuators.

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Another feature of the sol-gel process is that many of the available metal alkoxides of interest for thin film applications are extremely reactive toward moisture and must be stored and processed in controlled dry atmospheres. Their replacement with more stable reagents would greatly simplify the sol-gel processing of ceramic films.

Therefore, before all of these advantages can be realized, a number of processing parameters must be established. The choice of starting chemicals, solvents, and solution concentration, as well as handling conditions, solution reactions, and firing procedures, can all affect the phase assemblage and properties of the final material [41].

2.3.2 Fabrication of PZT precursors

The most commonly used starting chemicals for PZT synthesis are lead acetate trihydrate, zirconium tetra-n-propoxide, and titanium tetra-n-isopropoxide [41, 42]. Methoxyethanol (MOE) has been widely used as a solvent and stabilizer for preparing PZT precursor, because of its chelating properties and low viscosity. In more recent works, this toxic product has been substituted by less hazardous solvents, such as propanediol, acetic acid, acetone, and ethanolamine, and they are also effective for preparing PZT [43,44].

2.3.2.1 Chemicals used for sol-gel processing

Some commonly used chemicals for sol-gel processing are listed in Table 2-3.

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Table 2-3. Chemicals used in literatures.

Liter No/ year	Pb-source	Zr-source	Ti-source	Solvent
[43]/1990	Lead acetate trihydrate	Zirconium tetra(n-butoxide)	Titanium tetraisopropoxide	Diethanolamine, isopropanol
[45]/1991	Lead 2-ethylhexanoate	Zirconium tetra-n-butoxide	Titanium tetraisopropoxide	
[46]/1991	PbAc ₂ •3H ₂ O	Zr-n-butoxide	Ti-n-butoxide	Methoxyethanol
[47]/1992	Pb-acetate	Zr-tetra-n-butylate	Ti-tetra-iso-propylate	Methoxyethanol HNO ₃ /H ₂ O
[48]/1992	Pb(CH ₃ CO ₂) •3H ₂ O	Zr(C ₃ H ₇ O) ₄ Zirconium propoxide	Ti[(CH ₃) ₂ CHO] ₄ Titanium isopropoxide	Acetic acid
[34]/1993	Lead acetylacetonate	Zirconium <i>n</i> -butoxide	Titanium isopropoxide	2-methoxyethanol
[49]/1993	Lead Acetate Trihydrate	Zirconium tetra propoxide	Titanium tetra isopropoxide	2- Methoxyethanol + 2 mol water
[50]/1995	PbAc ₂ •3H ₂ O	Zr(OC ₃ H ₇) ₄	Ti(OC ₄ H ₉) ₄	CH ₃ OC ₂ H ₄ OH
[51]/1995	Lead acetate trihydrate	Zr(OC ₃ H ₇) ₄ propanol	Ti(OC ₃ H ₇) ₄ propanol	acetylacetone
[52]/1996	Lead Acetate Trihydrate	Zirconium <i>n</i> -propoxide	Titanium diisopropoxide Ti(OC ₃ H ₇) ₂ (CH ₃ C OCH-COCH ₃) ₂ Titanium diisopropoxide bispentanedionate	Propanediol butanediol pentanediol
[53]/1996	Pb(CH ₃ COO) ₂ •3H ₂ O	Zirconium <i>n</i> -propoxide	Titanium diisopropoxide bispentanedionate	1,3 propanediol HO(CH ₂) ₃ OH
[54]/1999	Pb(CH ₃ COO) ₂ •3H ₂ O	Zr(OCH ₂ CH ₂ CH ₃) ₄	Ti(OC ₃ H ₇) ₂ (CH ₃ C OCHCOCH ₃) ₂	CH ₃ COCH ₂ COC H ₃ acetylacetone
[37]/2000	Lead acetate trihydrate	Zr propoxide (70%)	Ti isopropoxide	Acetic acid
[55]/2000	Lead Acetate Trihydrate	Zirconium <i>n</i> -propoxide	Titanium diisopropoxide bisacetylacetonate	2,4-pentanedione and 1,1,1-tris(hydroxymethyl)ethane
[56]/2000	Lead Acetate Trihydrate	Zirconium acetylacetone	Titanium isopropoxide	Acetylacetone / 2-methoxyethanol

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2.3.2.2 Some important solvent

2.3.2.2.1 Methoxyethanol (MOE) [53, 55]

The first sol-gel techniques for producing PZT gels and films were reported in the mid-1980s [57]. Routes based on methoxyethanol (MOE) solutions of lead acetate trihydrate, titanium propoxide, and zirconium propoxide had found widespread uses. Following this route, PT, PZT and PLZT films were successfully prepared. The proposed structures of bimetallic complexes containing lead and titanium stimulated many research works from then on. Attempts were made to synthesize and characterize precursors containing the metals in the desired ratio closely bonded together. Further links between the heterometallic units are established during condensation/gelation. Many works were done to increase the film thickness and quality by the hydrolysis conditions (amount of water, catalyst, complexing agents). It turned out that, in most cases, little or no water led to the best results.

The MOE route yields high-quality PZT films, but the limiting thickness for crack free films is usually $< 0.1 \mu\text{m}$ for single-layer samples on silicon substrates. Thicker single layer cracks, mainly as the result of volume shrinkage on converting the low-density amorphous gel to a crystalline PZT film, and also because of thermal expansion mismatches between the film and substrate. Below a critical thickness, $0.1 \mu\text{m}$ in the case of the MOE route, the mechanical constraint of the substrate is sufficient throughout the film to inhibit lateral shrinkage and avoid crack formation. For the fabrication of films thicker than $0.1 \mu\text{m}$, a multiple deposition and pre-firing procedure above 200°C must be repeated. Some researchers have found that, when commonly called "acetylacetone-modified" titanium precursors are used, it is possible to repeat each deposition 10 times without cracks forming, thereby enabling PZT

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films up to 1 μm to be prepared on the platinized silicon wafer after final firing at 600–700°C [39].

For certain PZT film applications such as piezoelectric actuators and electromechanical sensors, it is desirable to prepare film up to 10–50 μm thick. The MOE route is not suited for this purpose and hence alternative sol-gel routes have been investigated with the aim to increase the limiting thickness for crack-free single-layer and multi-layer films.

2.3.2.2.2 Acetic acid [52]

Sol-gel process using acetic acid has been reported to produce significantly thicker single-layer PZT coatings than using methoxyethanol [38,44]. A 2.5 μm thick single-coating has been demonstrated by this acetic acid route but the film appeared to be rather porous. The acetic acid route does not involve any reflux reactions; instead, after dehydration of a lead acetate solution, the solution containing titanium and zirconium alkoxides are mixed by ultrasonic agitation. After that, glycerol or ethylene glycol is added before film coating to prevent cracking [48] and adjust viscosity [50].

2.3.2.2.3 Propanediol (Diol) [52, 53, 58]

Researchers have attempted a diol sol-gel process, in which α , ω -dihydroxyalkanes are used in conjunction with "acetylacetonate-modified" titanium and zirconium propoxide starting reagents, namely presynthesized $\text{Ti}(\text{OC}_3\text{H}_7)_2(\text{CH}_3\text{COCHCOCH}_3)_2$ and $\text{Zr}(\text{OC}_3\text{H}_7)_2(\text{CH}_3\text{COCHCOCH}_3)_2$. It has been reported that in a standard procedure, it is possible to fabricate high-quality 0.5 μm single-layer films on a platinum coated silicon substrate, and films of up to 10 μm can be made using the multilayer deposition technique.

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In contrast to other sol-gel routes, the diol system does not rely on hydrolysis-condensation reactions within the initial sol to form the polymeric species that lead to gelation. The advantage would be that the sol-gel precursor does not inherently have to be moisture sensitive; in fact it could often be readily handled in air as well. In the diol route linear polymers are essentially proposed, although there may also be some hydrolytic M-O-M cross-linking arising from the water of the hydrated lead acetate. The increase in the limiting thickness of crack-free layers could therefore be attributed to the linear structure. It may allow the chains to rearrange during drying and shrinkage of the gel layer and make it a more compliant gel system. However, further studies, including an assessment of pore-size distributions in gels during drying and thermolysis, are required to fully explain the factors governing the limiting thickness of PZT films prepared by the different sol-gel routes.

2.3.3 PZT films deriving by spin-coating

While the deposition procedure (spinning, dipping) remains unchanged, it is noticed that the heating procedure as well as the substrates used is in addition to the sol chemistry of dominating influence on resulting film microstructure. Especially the concept of rapid thermal annealing (RTA) is successful in improving the quality of the films, such as reduction of film-substrate interactions, kinetic control of undesired intermediate phases, control of perovskite nucleation and crystallite growth [59, 60].

2.3.3.1 Crack in films

A drawback of the sol-gel method for thin film fabrication is the occurrence of film cracking brought by stresses arising during the thermal conversion of the organic-based gel into a ceramic film. Generally, the thinner the film, the lower the incidence of film cracks. This is because adhesion at the film-substrate interface is

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sufficient in the thinnest coatings to suppress lateral shrinkage throughout the film. As the thickness increases, a critical value is reached above which cracking becomes unavoidable.

The parameters influencing the maximum thickness of crack-free films include gel chemistry and gel structure, pore size, substrate-film adhesion, heating conditions, and differences in thermal expansion coefficients between film and substrate. Moreover, the use of clean room processing, wherever possible, is advisable in order to avoid cracks and other flaws originating from particulate contamination [52,61].

2.3.3.2 Other features

2.3.3.2.1 *Density*

It is reported that the porosity of the films strongly depends on the film thickness. Films with thickness below 0.2 μm show a fully dense structure, whereas films with thickness exceeding this limit show a homogeneous nano-porosity. It is assumed that during the heating process a densification of the surface occurs within a short time. This prevents the release of solvents and decomposition products of organic compounds, which are still present in the film. Thus, the remaining porosity is dependent on the film thickness and the heating conditions.

2.3.3.2.2 *Orientation*

In thicker films, nucleation and grain growth start both on the surface and on the substrate, even though heterogeneous nucleation is expected only on the substrate. A temperature gradient inside the film with a higher temperature at the film surface, however, leads to simultaneous nucleation and grain growth on the surface as well as on the substrate. On the contrary, the temperature gradient is smaller in thin films, so that nucleation predominantly occurs on the substrate or on the underlying PZT.

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Hence the orientation of the grains in the first layer may be maintained in subsequent layers.

2.3.4 Crack-free films on Pt/Si substrate

In both the dried and fired gels, the internal tensile stress has the most significant impact on the film; and this should clearly be reduced to avoid cracking. This may be done by either chemical or physical means [62].

2.3.4.1 Chemically modified

In the case of drying, since the internal tensile stress of the gel film is produced by high pressure of the liquid in the gel, the probability of cracking can be reduced by decreasing this pressure. Chemically it can be achieved by reducing the affinity between the liquid and the solid network, and by increasing the pore size. Cracking is reduced by adding long-chain alcohols or polyethylene glycol into the solution. This reduces the force imposed on the solid network. After drying the gel film has a lower internal tensile stress. However, since coarse structures require higher firing temperatures and longer annealing time, the microstructure and electrical properties can be degraded by this route [63].

The organic modifiers (e.g. methyl, ethyl or phenyl groups) are considered to reduce the three-dimensional cross-linking of the silanol groups, giving rise to increased coating layer flexibility, *i.e.*, preventing the formation of cracks in the coating. Moreover, the nonpolarity of the organic modifiers is assumed to provide a hydrophobic effect, thus reducing the capillary force during drying of the coating [64].

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2.3.4.2 Heat treating

During the drying and firing procedure of films fabrication, approximately 70 wt% of the starting materials in gels are evaporated or calcined away, and the final ceramic film has to adjust at least to a thermal cycle in which the film on substrate is cooled from the crystallization temperature to ambient [63].

After formation of a gel film on a substrate, commonly used firing schedules are shown in Figure 2-3. If the film is thin (final thickness $< 0.3 \mu\text{m}$), it is often placed directly on a surface heated to $T_2 = 400^\circ\text{C}$ until decarbonization and oxidation has occurred, and is then annealed at a higher temperature. The firing schedule is as shown in Figure 2-3(a). For films of thickness in the micron range, the firing schedule shown in Figure 2-3(b) is preferred. The films is initially dried slowly to about $T_1 = 285^\circ\text{C}$, Then rapidly fired to $T_2 = 400^\circ\text{C}$, followed by a final anneal at a temperature T_3 from 450°C to 650°C depending on the materials and the substrate. $T_1 = 285^\circ\text{C}$ corresponds to the decomposition temperature of lead acetate, a key ingredient of most sol-gel solutions for PZT. While at $T_2 = 400^\circ\text{C}$ most organic components of the film would be pyrolyzed and oxidized, and it would be leave an amorphous inorganic layer. A rapid temperature rise between T_1 and T_2 would be useful.

Stresses that lead to cracking of the film may occur during (i) drying, (ii) firing, (iii) annealing and crystallisation, and (iv) on cooling. It is found that the most critical time is often in the stages (ii) and (iv).

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Figure 2-3 Firing schedules for sol-gel films: (a) for thin films with thickness $< 0.3\mu\text{m}$ and (b) for thick films of thickness in the micron range.

2.3.4.3 Buffer layer

G. Yi *et al.* [48] deposited a thin alumina layer between the substrate and the subsequent PZT films to compensate the thermal mismatch between the PZT films and substrates so that it can play a significant role in avoiding cracks. The film surface was smooth in the sub-micro rangel for a film thickness of up to several microns. PZT films grown in this way showed a smaller remnant polarization and a larger coercive field than expected from the equivalent bulk ceramics.

2.3.4.4 Composite films with powder loaded

Barrow [65] *et al.* developed a sol-gel based ceramic-ceramic 0-3 composite coating technique by dispersing ceramic powders into the sol-gel solution to form a thicker film. The resulting solution can be spin-, dip- or spray- deposited or painted onto a substrate, fired and annealed in the same manner as the conventional sol-gel. The composite solution is coated on a substrate in a manner similar to that for a

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conventional sol-gel. The fired film is a composite material consisting of a ceramic thin film matrix with bulk ceramic powders dispersed throughout in the solution. The ceramic powder and the sol-gel derived phase bond together during firing. The particles suspending in the sol-gel solution affect the thickness of single deposited coating. Individual layers (3 ~4 μm thick) can be achieved with this sol-gel composite. By depositing multiple layers, coating of total thickness from 3 to 100 μm have been obtained on various substrates. Final annealing of the multi-layer coating at 600°C crystallizes the sol-gel and creates a strong bond between the sol-gel and the powder.

The success of this new process to deposit PZT films up to several tens of microns is because of sol gel films strongly adhere to oxide surfaces on both individual crystallites and the substrate, particularly if this has an oxide layer, alumina for example. This bond is due to the presence of functionalized, hydroxyl groups on the surface of the oxide. The polymer species or macrocluster that form in the sol gel matrix solution during hydrolyzation of the organometallic precursors are able to react with these surface hydroxyl groups and form strong bonds. Therefore, when the PZT powder is mixed into the sol gel matrix solution, strong bonds are formed between the sol gel, the ceramic powders, and the substrate. In other words, this thick film process is actually making up a matrix surrounding the ceramic particles. It is just like the relationship between mortar and brick in a wall. The fact that slurry derived PZT films do not crack during processing can be mainly attributed to two factors: (a) there was a high quantity of ceramic particles in the final film. Therefore, the percentage of sol gel in the film was decreased accordingly and less shrinkage occurred when the film was processed. (b) the film bonded into a strong space network, with a sol gel thin film bonded between ceramic particles, making it less likely to have macroscopic

Chapter 2 Background

cracks in the film during processing due to the largely reduced stress and stress distribution at concentrated points.

However, the crack-free PZT thick films derived by this composite process have poor mechanical and electrical properties, mainly due to their porous microstructure. The coarse surface on the film has to be polished before device application. Therefore, fabricating crack-free, dense and homogeneous PZT thick films with large area by sol-gel techniques is still challenging.

2.4 MEMS type piezoelectric devices

2.4.1 Piezoelectric films for MEMS type device

Piezoelectric films have been used in a variety of MEMS type devices. Of available piezoelectric materials, the three most widely studied piezoelectric films for MEMS have been zinc oxide (ZnO), aluminum nitride (AlN), and PZT [66]. The main considerations for piezoelectric materials to be used in MEMS applications are their processing compatibility with silicon and their piezoelectric response. The properties of these three materials are compared in Table 2-4.

ZnO was the first piezoelectric films used in commercialized TV surface-acoustic-wave (SAW) filters because of its high piezoelectric coefficient (compared to non-ceramic materials) and simplicity of preparation. AlN, another promising piezoelectric material, has a piezoelectric coefficient that is lower than ZnO, but its high acoustic velocity makes it attractive for high frequency devices (in the GHz range). In addition, its stability at high temperatures and humidities makes it compatible with silicon processing, in which diffusion, annealing, and implantation are required.

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PZT was first developed in bulk ceramics and was primarily used for sensor and actuator applications. During the past decade, the fabrication and characterization of PZT films have been investigated by many researchers [66]. Its high electromechanical coupling and piezoelectric constant, which are an order of magnitude larger than ZnO and AlN, have drawn great attention for MEMS sensor and actuator applications. Table 2-5 summarizes the measured piezoelectric constant of PZT films with compositions near morphotropic phase boundary (MPB). The measured values are distributed over an extraordinarily wide range for films of nominally the similar composition. Some of the spreads of values arise from the specific microstructure of the films, and some are due to different measurement techniques used.

2.4.2 Piezoelectric MEMS type devices

MEMS type piezoelectric devices based on PZT films, such as force sensors [67], pressure sensors [68], accelerometers [69], micropositioning actuators [70], micromotors [71], and micropumps [72], can be found in the literature. Most of these device applications are sensors and actuators, and are based on some form of a piezoelectric bimorph. The piezoelectric film is grown on a bulk substrate, usually silicon with some other structure film deposited on it, such as amorphous silicon nitride. The substrate material is then thinned beneath the device active area, leaving a very thin (few micron thick) composite cantilever or diaphragm. When an electric field is applied perpendicular to the cantilever/diaphragm plane, device actuation occurs via in-plane strain of the piezoelectric (d_{31} actuation).

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Table 2-4. Properties of piezoelectrics.

Materials	ZnO	AlN	PZT
Form	Single crystal	Single crystal	Polycrystalline film
Piezoelectric constant: d_{33} (pC/N)	12	3.9	117
Force, current response: e_{31} (C/m ²)	-0.7	-1.0	-12
Coupling coefficient: k^2 (%)	6	11	19

Table 2-5. Piezoelectric constant measurements of PZT films at MPB.

Reference	d_{33} (pm/V)	d_{31} (pm/V)	Measurement technique	Comments
[73]PZT53/47		-40	1	Sol-gel films
[74]PZT53/47		-100	2	Sputtered films, (001)-oriented, no poling
[75]PZT53/47	220	-88	3	Sol-gel films, measured with DC bias
[76]PZT53/47	180		3	Sol-gel films, measured at varying DC bias, frequency
[77]PZT53/47	110		3	Sol-gel films, measured at varying DC bias
[25]PZT52/48	194		4	Sol-gel films, poled at room temperature for 2 min
[79]PZT52/48	200- 350		4	Sol-gel 12 μ m thick, (100)- oriented, poled at room temperature
Remarks	1 = stressing a membrane and measuring charge; 2 = measured expansion of film released from substrate; 3 = single-beam laser interferometer; 4 = double-beam laser interferometer.			

CHAPTER 3 EXPERIMENTAL

PROCEDURE

A novel hybrid processing technique based on sol-gel composite, in which fine PZT particles were dispersed into the sol-gel matrix solution to make films, has been developed in this thesis research. With this new technique, it is now possible to coat dense, uniform and crack-free PZT composite thick films of up to tens of microns in thickness on platinum-coated silicon substrates.

As the hybrid processing technique is a combination of high-energy ball-milled particles and sol-gel process, the processing technique of high-energy ball milling and fabrication of PZT precursor are presented in this chapter. This chapter also contains a description of the equipment employed and the analysis used to determine the crystallization and electrical properties of films. The experimental approach is described as:

- 1) Hybrid processing technology: high-energy ball milling and sol-gel process;
- 2) Crystallization and microstructure characterizations;
- 3) Dielectric and ferroelectric properties characterizations.

3.1 Hybrid processing technology

3.1.1 High-energy ball milling: treatment of PZT powders

The high-energy ball milling process has been successfully used to obtain nano-sized oxide powder particles. In this thesis, with a Frisch Pulverisette 5 planetary ball-milling machine, high-energy ball milling technique was applied to reduce the particle size and to promote the dispersion of particles in sol-gel solution.

Chapter 3 Experimental procedure

A closed container with tungsten carbide (93 wt% WC + 6 wt% Co, $\rho = 14.75 \text{ g/cm}^3$) vials and balls was chosen. The vial has a volume of 250 ml with an inner diameter of 75 mm and the balls have diameters of 10 mm and 20 mm.

Dry milling method was employed to obtain nano-sized particles. Commercial PZT powder (APC850) was used with a mass ratio of 1: 20 to balls. Excess 5 wt% lead oxide was added to compensate the lead loss. The milling speed is set at 200 rpm for dry method and 150 rpm for wet method. The milling was carried out in 30 minutes cycles with 20 minutes of milling followed by 10 minutes of pause to prevent the milling system from overheating with prolonged milling. Powders were collected after milling for certain hours, namely 20 or 30 hours, respectively.

3.1.2 Sol-gel process: xerogel precursor and sol solution

The sol-gel matrix solution used for the hybrid sol-gel composite coatings of interest was based on lead zirconate titanate $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ (PZT 53/47). This composition lies in the morphotropic phase boundary (MPB) region of the PZT phase diagram. It is well known that at room temperature a coexistence of tetragonal and rhombohedral structures occur on this boundary, which leads to the maximum values of the dielectric constant and the piezoelectric coefficients of PZT ceramics [80].

Sol-gel processes generally employ metal alkoxide precursors which are often water sensitive and need to maintain close control over hydrolysis and condensation reactions. Polymeric mixed metal alkoxide species are formed to serve as molecular building blocks for the subsequent development of a crystalline structure. There are five basic steps involved in the sol-gel process:

- 1) Dissolution and reaction of the cation precursors in a suitable solvent to produce a stock solution;

Chapter 3 Experimental procedure

- 2) Adjusting the solution characteristics including viscosity, mole ratio, and solid content;
- 3) Film deposition;
- 4) Low temperature heat treatment for organic pyrolysis;
- 5) High temperature annealing for film densification and crystallization.

A chelate method, which was developed previously in our laboratory [81], was used to prepare PZT xerogel for sol-gel solution fabrication. “Chelate” method is essentially a molecularly modified alkoxide precursors (MMAP) approach [82] to create moisture tolerant metal-organic precursors by changing the molecular structure of the precursor. The moisture tolerant precursors created in this way can be used to prepare stoichiometric and stable sols. In this thesis, acetylacetone was used as a chelating agent for titanium isopropoxide.

A brief description of xerogel-MOE solution preparation is outlined below. The raw chemical compounds used in this thesis are listed in Table 3-1. The xerogel preparation procedure for PZT sol-gel solution is schematically shown in Figure 3-1.

1. Chelating the titanium isopropoxide with acetylacetone in molar ratio of 1: 1 by heating and stirring the mixture at 80 °C for 10 minutes. Before heating, titanium isopropoxide was slowly dripped into the acetylacetone with a transfer to avoid the effect of moisture as best as can. This reaction is an exothermic reaction so that a white fume was observed during stirring. The chelated titanium isopropoxide was stable even in open air for a long period. By replacing one isopropoxide group with acetylacetone, the hydrolysis speed of the modified titanium isopropoxide was greatly reduced [83]. This step was the key process of the solution preparation.

Chapter 3 Experimental procedure

2. The lead acetate trihydrate with 10 wt% excess was added into the modified titanium isopropoxide solution. Ti-Pb mixture was obtained by stirring at 120°C for 10 minutes. After lead acetate trihydrate was added, oil-like coacervation was observed, which means the hydrolysis of the partially stabilized titanium isopropoxide occurred.
3. The zirconium acetylacetonate was dissolved into the Ti-Pb mixture. By stirring at 110°C for 30 minutes, a yellow clear sticky solution was obtained.
4. Solution was placed into a vacuum drying oven to remove volatile products under reduced pressure at 100°C for more than 4 hours and xerogel, a porous light yellow solid precursor powder, was resulted. By dissolving 10 wt% ~40 wt% xerogel into 2-methoxyethanol solvent at 125°C with stirring for 30 minutes, yellow clear sol was obtained. Shade of yellow depended on the concentration.
5. The resultant sol was filtered into storing amber bottles with 0.1 µm Teflon micropore filter and then aged in a desiccator for 24 to 48 hours.

Table 3-1. Precursor and solvent chemicals used for PZT 53/47 sol-gel processing.

Chemical	Formula	Molar mass	Purity
Tetraisopropyl titanate	$[(CH_3)_2CHO]_4Ti$	284.22	97%
Zirconium acetylacetonate	$[CH_3COCH=C(O-)CH_3]_4Zr$	487.66	98%
Lead acetate	$(CH_3COO)_2Pb \bullet 3H_2O$	379.33	>99.5%
Acetylacetonate	$CH_3COCH_2COCH_3$	100.12	>99.0%
2-methoxyethanol	$CH_3OC_2H_4OH$		
1,3-propanediol	$HO(CH_2)_3OH$		

Chapter 3 Experimental procedure

Figure 3-1. Flow chart of PZT 53/47 xerogel preparation process using chelating method.

3.1.3 Spin-coating of $\text{PbZr}_{0.53}\text{Ti}_{0.47}\text{O}_3$ films

In this thesis, most of the substrates used were (100) single crystal silicon wafer, 4 inches in diameter, coated with silicon dioxide, titanium layer, and platinum bottom electrode successively. Thickness of each layer was 500 nm, 150 nm and 150 nm respectively. Platinum is one of the most popular noble electrode materials because it has excellent oxidation resistance. Titanium layer acts as an adhesion layer between platinum and underlying silicon dioxide.

Chapter 3 Experimental procedure

Prior to use, the as received substrates were cleaved into pieces ~1 inch in width and 1 inch in length before coating. All substrates were soaked in acetone at 80°C and rinsed with isopropanol to remove oil, organic contaminants and dust from substrate surface. The substrates were finally rinsed with de-ionized water in the dump riser for four cycles and then dried with dry nitrogen.

Using a photo-resist spinner, PZT film was deposited with spin-coating process on substrate at a speed of 3000 rpm for 30 seconds (if not otherwise specified). By placing the coated film onto a hotplate directly, each layer was dried at 250°C and pre-baked at 500°C for 2 minutes, respectively, before next layer was deposited. This procedure was repeated till desired thickness was reached. Firing was carried out in a pre-heated Thermolyne 47900 resistive furnace at 550°C for 2 minutes for every 3 coated layers. Finally the final multiplayer film was annealed at 550°C to 800°C for 30 minutes, by directly inserting the samples into a preheated furnace in air or oxygen atmosphere. If not specifically stated, the data presented in this thesis was obtained from films annealed in air. Selected samples were annealed in oxygen-rich atmosphere to examine their microstructure and properties.

All preparation steps were performed in a glove box filled with nitrogen with a relative humidity controlled between 40 ~50%.

3.2 Crystallization and Microstructure Characterization

3.2.1 Thermal analysis

The thermal requirement and considerations lead to the preference for the sintering procedure. A Perkin Elmer thermogravimetric analyzer (TGA-7) and a differential thermal analyzer (DTA-7) were used in this thesis to examine the thermal behaviors of the formulated PZT xerogel and sol-gel solution at different temperatures.

Chapter 3 Experimental procedure

The temperature range was from room temperature to 800°C and the heating rate was 2°C per minute.

3.2.2 Phase identification

The phase and structure of samples after heat-treatment were studied at room temperature using a Rigaku RINT 2000 diffractometer with a thin film attachment cum Ultima+ wide-angle goniometer. CuK α radiation source of 1.54056 Å at 50 kV 20 mA was chosen as the light source. The scan range of 2θ was from 20° to 60°. The detector moved at rate of 2° per minute, and collected the data every 0.1 second.

For PZT thin films, a theta fixed angle of 0.5° was chosen to minimize the signal of platinum bottom electrode and get more information of the measured films.

3.2.3 Microstructure characterization

The samples were examined both in plan view and in cross-section using a JEOL JSM 6340F Field Emission Scanning Electron Microscope (FESEM) with an accelerated voltage of 5 kV. A thin layer of gold was coated for 15 ~20 seconds to avoid the electric charging of the samples.

The thickness of the films was measured through the cross-sectional SEM image or using a SLOAN DEKTAK 8000 type surface profilometer.

3.3 Electrical Characterization

3.3.1 Fabrication of PZT capacitor for characterization

For the purpose of characterization of the ferroelectric and dielectric properties, a metal-ferroelectric-metal (MFM) capacitor device was fabricated by PZT films etching and electrode coating described as followed. A schematic of the MFM test structures is illustrated in Figure 3-2.

3.3.1.1 Bottom electrode contact opening

Electrical contacts with the bottom platinum electrode had to be made. PZT films at a corner on the substrate were carefully etched off to reveal the bottom platinum by dipping it into an etchant partially. The etchant was made of de-ionized water, hydrochloric acid HCl and hydrofluoric acid HF at a ratio of 50: 50: 0.1. An etching rate of 1 $\mu\text{m}/\text{min}$ was approximately realized at room temperature. After etching, samples were rinsed in de-ionized water, dried in dry nitrogen, and then inspected under an optical microscope.

3.3.1.2 Deposition of top electrode

Gold or platinum top electrode was deposited on the PZT films successively by either electron beam evaporation or sputtering technique. Silicon shade mask or lift-off process was used to define the shape of the top electrode. 5 nm-thick titanium and 250 nm gold film were deposited sequentially in the $0.77 \times 0.77 \text{ mm}^2$ square openings.

The exact size of the top electrode was measured by an optical microscope with a scaled attachment before electrical properties characterization.

The MFM capacitor was placed in a vibration-proof microprobing station and measurement was conducted by microprobe to the bottom and top electrodes.

Chapter 3 Experimental procedure

Figure 3-2. A Schematic of the MFM test structures.

3.3.2 Ferroelectric and dielectric properties

Hysteresis loops (P-E) were measured using Precision Pro Ferroelectric Analyzer (Radiant Technologies RT66A, Albuquerque, NM) with high voltage interface at 1 kHz. The duration was set as 1 ms for P-E hysteresis measurement.

Low field measurements of the dielectric constant and dielectric loss were carried out using a HP4284A Precision LCR Meter (Hewlett-Packard, Palo Alto, CA). The AC oscillation level of 1 kHz was set at 50 mV. The parallel circuit mode was employed during measurement. The leakage currents of the films were measured by a HP 4155B semiconductor parameter analyzer.

CHAPTER 4 A NOVEL LOW TEMPERATURE PROCESSING APPROACH USING HYBRID SOL-GEL COMPOSITE TECHNIQUE

4.7 Introduction

Over the years, PZT ceramics have been prepared by the traditional mixed oxide method in which the solid-state reaction of mixed metal oxides occurred. Such reaction often leads to compositional and structural inhomogeneities, such that repeated calcinations and grinding steps, as well as much higher heating schedules are required to overcome large diffusion distances. Therefore, this method has been gradually updated by suitable chemical processes. For example, sol-gel processing has attracted great attention because of its low processing temperature, better control over stoichiometry and chemical homogeneity. However, the excessive cost and special handling of extremely moisture sensitive alkoxide precursor preclude the wide adoption of this technique for routine ceramic synthesis. Furthermore, films derived by the sol-gel processing technique have a typical thickness limitation of 1 μm , above which films will have cracks or peel off from the substrate due to the stress in films. Though thick films with thickness of tens of micrometer can be deposited by the screen-printing and tape casting techniques, the PZT thick films deposited by these methods have low density and need high temperature sintering, which is not compatible with the silicon micromachining process. Accordingly, some features of

the sol-gel processing technique, which can decrease the processing temperature, are looked forward to being introduced into these techniques. Moreover, due to large driving force and short diffusion distance, there is a narrow temperature interval between the crystallization and densification temperature. Electroceramics prepared by the nano-composite method therefore have density better than the conventional monophasic sol-gel based process. In other words, dense materials, both in films and bulk ceramics, can be readily obtained at a low temperature from nano-sized starting precursors. In view of the above advantages, by combining sol-gel processing and nano-composite techniques, an attempt has been made to prepare and evaluate PZT piezoelectric material with fine grains crystallized at a relatively lower processing temperature.

A novel hybrid technique for low temperature processing based on nano-sized powders and homogenous matrix of sol-gel precursor composite has been developed in this thesis. The key of this technique is the combination of sol-gel precursors and nano-sized particles. If the calcinated sol-gel precursor has the same composition as the nano-sized powders, the mixture is called homogenous matrix; therefore, the resultant material will have a single phase. On the other hand, if the precursor is mixed with nano-sized powders with different composition, multiphase composites can be produced from the heterogeneous matrix. Figure 4-1 outlines the features of this hybrid technique. Different applications of this approach could be applied by utilizing its respective merits. For example, low temperature sintering of screen-printing films could be obtained since the sol-gel precursor used as a binder between ceramic particles. This will be particularly of interest to multilayer devices because cheaper internal electrode paste could be used during the screen-printing process.

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Moreover, the simplicity of this approach is useful to most of the bulk ceramic process.

In this chapter, details of this hybrid sol-gel composite processing technique are described, and its applications to bulk ceramics and screen-printed thick films are also discussed.

Figure 4-1. Illustration of the features of the hybrid process using nano-sized powders.

4.2 Low crystalline temperature of the sol-gel precursors

4.2.1 Thermal properties of the xerogel precursor

The behavior of the PZT 53/47 xerogel precursors at different temperature was examined using Thermogravimetric analysis (TGA) and differential thermal analysis (DTA).

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TGA is a thermal analysis technique which measures weight loss of a sample during a thermal program. This can be used to determine the temperature at which organic components of the film are decomposed. Moreover, from this data it is possible to obtain a derivative thermogravimetric plot (DTG). As a sample loss weight due to evaporation or other reactions, internal stresses can develop within films and cause failures such as cracking. TGA and DTG are useful in determining temperatures at which the rate of weight loss is maximum. It is quite useful to determine the heating sequence during films deposition.

DTA measures the temperature of a sample relative to that of a reference material heated at the same rate. Endothermic and exothermic reactions undergone by the sample at different temperatures indicate whether the reaction absorb or release energy, providing some useful indication as to the type of reaction taking place. It shows as negative or positive peaks respectively on the DTA plot.

Since sol-gel solution has a very high solvent to PZT ratio, most of the weight loss and thermal reactions will happen at a low temperature less than 150°C. To increase the resolution of the TGA and DTA at higher temperature, xerogel samples before dissolved into solvent were used for thermal analysis.

Figure 4-2 shows the typical DTA and TGA results for the formulated xerogel samples heated at a rate of 2°C/min. Figure 4-3 is a comparison between the rate of weight loss (derivative of the TGA curve, or DTG) and the DTA data for the PZT 53/47 xerogel.

There are two main stages observed in the decomposition reaction. In the temperature range of 100–300 °C, the samples show several exothermic peaks in the DTA curves. The TGA curve presents marked weight losses in this temperature region, which is consistent with the DTA result. By combining the two curves, the

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DTA peaks in this temperature range can be attributed to the evaporation of solvent as well as combustion and decomposition of organics. The TGA curve shows that about 35 wt% of the xerogel sample weight was lost before 300°C. According to the thermal analysis, the film drying temperature in the process of deposition PZT films was chosen at 250°C to remove the organic components from as-coated gel films.

In the temperature range of 300~500 °C, two exothermic peaks are observed in the DTA curves of all the samples. In this region, the samples present a less gradual weight loss with platforms. It is interesting that there is an exothermic peak centered at 350 °C, but there is no corresponding weight loss observed from the DTG curve. It means that the weight loss in this temperature range is either beyond the detection limit of the TGA or that no weight is lost and the release of energy is due to the internal reorganization of components, possibly the formation of pyrochlore phase. The higher exothermic peak centered at 435 °C is due to PZT crystallization. A slight weight loss about 3wt% corresponds to the transition from $A_2B_2O_{7-x}$ pyrochlore phase to ABO_3 perovskite phase. Such a low crystallization temperature of xerogel, lower than 500 °C, is a very good feature for getting good quality PZT ceramic at low processing temperatures.

At temperature above 500 °C, as the dashed vertical line shown in Figure 4-3, the chemical reaction is complete. Approximate 62 wt% of inorganic composition is remained from the fabricated xerogel as shown in TGA curve. This suggests that firing of the xerogel requires temperature could be as low as 500 °C to get a preliminary crystalline phase in the materials.

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Figure 4-2. DTA and TGA data of PZT53/47 xerogel carried out at a heating rate of 2°C /min in air.

Figure 4-3. Comparison between DTG and DTA results. The DTG data is a derivative of TGA plot.

4.2.2 Phase development of xerogel precursor

The crystalline phases in the PZT53/47 xerogel developed during annealing were identified by X-ray diffraction (XRD). The measurements were carried out by a Rigaku X-ray RINT 2000 diffraction system with standard sample holder using CuK α radiation at 25kV. The samples were detected in 2θ from 15° to 75° with a sweep rate of $2^\circ/\text{min}$. The X-ray diffraction patterns of xerogel heat-treated at 300°C , 400°C , 500°C , 600°C and 700°C for 30 minutes in air are illustrated in Figure 4-4.

The xerogel heat-treated at 300°C is found to be amorphous. For the sample treated at 400°C , two strong peaks centered at 29.6° and 31.2° are observed. It is found from the database that the diffraction peak at 29.6° is the strongest peak in XRD pattern for the pyrochlore-type phase. The other peak could be attributed to the transformation of perovskite phase. The pyrochlore phase appeared in PZT xerogel is of a cubic structure, with a general formula $\text{A}_2\text{B}_2\text{O}_{7-x}$. With further increasing temperatures, the pyrochlore phase gradually disappeared and the perovskite phase structure formed in abundance. According to the XRD pattern of xerogel treated at 700°C , perovskite-prominent structure remained in the resultant materials.

It is well known that the pyrochlore structure is a metastable intermediate phase before perovskite structure is formed. From the XRD patterns, traces of the perovskite phase can be found down to 400°C in xerogel, which is quite close to the formation temperature of pyrochlore phase. It may be attributed to that, in sol-gel processing technology, the precursors are mixed at a very fine scale (nm level) thus the diffusion distances are relatively smaller compared to those encountered in traditional mixed oxide synthesis of ceramics. Thus even at a fairly low temperature (400°C), it is possible to nucleate perovskite phase at nano scale that may not be detected by X-ray diffraction technique. In other words, it may not be necessary to

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convert the originally amorphous xerogel into a pyrochlore phase before the perovskite formation. A direct amorphous to perovskite phase transformation is possible.

As a result, if the heating rate is fast enough, the amorphous PZT xerogel might crystallize into perovskite phase directly without or with minimum pyrochlore phase formation. If the heating rate is slow, on the other hand, phase evolution with increasing processing temperature for PZT xerogel generally proceeds from an amorphous phase to a pyrochlore-like intermediate phase then to perovskite [88-90]. The XRD results supported a mechanism for the formation of the perovskite, as discussed by Carim et al. [91]. The resulting material was a crystalline PZT with perovskite-type structure dominant.

Figure 4-4. X-ray patterns for xerogel heat-treated at different temperature for 30min.

4.3 Screen-printed thick film on Au/Al₂O₃ substrate

4.3.1 Experimental process

As discussed above, high-energy ball milling and sol-gel process techniques were employed into the screen-printing process for PZT53/47 thick films deposition. The flow chart of the thick film fabrication process is schematically shown in Figure 4-5.

The obtained thixotropic PZT paste is allowed to flow through the pattern on the screen by a rubber squeegee blade that traverses the surface of the screen at a controlled speed, and deposits on to the substrate.

4.3.2 Thermal properties of the PZT 53/47 paste

The thermal requirement and considerations lead to preference of the sintering procedure. After the mixing of sol-gel solution and PZT powder, some paste was collected out and dried at 110°C for 4 hours in vacuum chamber. The powder was obtained and readily used for DTA and TGA investigating. The temperature range was from room temperature to 1000°C at a heating rate of 2°C per minute.

Figure 4-6 shows the results of DTA and TGA analysis. The remarkable weight loss between room temperature to 350°C is due to solvent evaporation as well as organic combustion decomposition. It is consistent with the DTA result. For DTA curve, decomposition and combustion of the organic in the precursor are contributed to the two exothermal peaks before 400°C. A series of small exothermal peaks between 400°C to 600°C are due to the crystallization of pyrochlore phase, decarbonization of carbonate, and transformation of pyrochlore phase into perovskite phase in the PZT53/47 materials. A slight weight loss about 1wt% was observed in the TGA curve at this temperature range. An increasing weight loss above 850°C

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observed in the TGA curve can be attributed to the volatilization of lead from materials.

Figure 4-5. Flow chart of the PZT thick films fabrication using screen-printing process.

Figure 4-6. DTA and TGA analysis of dried PZT53/47 paste derived from sol-gel precursor and powder, at a heat rating of 2°C/min in air.

4.3.3 Microstructure of the PZT53/47 thick films on Au-Al₂O₃ substrate

The crystalline phase analyses of PZT53/47 thick films and ceramics after sintering were identified by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The investigations were carried out by Siemens D5000 diffractometer and a JEOL field emission-SEM.

The X-ray diffraction patterns for PZT thick film on Au/Al₂O₃ substrate screen-printed from paste mixed with nano-sized particles and sol-gel precursor solution is shown in Figure 4-7. Obviously, single perovskite structure could be obtained in thick film samples sintered at 650°C.

Figure 4-7. XRD pattern for PZT thick films on Au/Al₂O₃.

To understand the grain growth during sintering, PZT53/47 thick films on Au/Al₂O₃ substrate fabricated using screen-printing processing technology were investigated by FE-SEM technique. Figure 4-8 and Figure 4-9 show the surface morphologies and cross-section of thick films sintered at different temperature for 30 minutes: 650°C, 700°C, 750°C and 800°C.

It is observed that all the samples sintered at temperature ranging from 650°C ~ 800°C has a uniform and relative dense microstructure. The grains in the material contact with each other tightly; and there are no obvious pores detected. Compared with the results of screen-printed PZT thick films published before [78], the density in films was markedly increased. It could be mainly attributed to the nano-sized particles employed for the much larger driving force during the solid state consolidation.

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Particularly, samples sintered at the 650°C have an average grain size of 70 nm and nearly a granular structure. The uniformly distributed individual nano-sized particles prove that the agglomerates among the nano-size powder loaded have been completely eliminated in the matrix. At 700°C, the grains are slightly larger than those sintered at 650 °C but still less than 100 nm. The average grain size is sharply increased between 700°C and 750°C. As the average grain size increases, it is obvious that some added powders and sol-gel derived crystallites must shrink and disappear. The final submicron-sized grains are fully developed at 800°C. At this stage, a totally new homogeneous polycrystalline matrix has been formed, although it originally consists of powders and sol-gel derived phase. It is evident that if the composition of the powder and the sol-gel derived phase are the same, the growth of the new generation grains will consume both the original phases.

As a result, dense thick films on Au/Al₂O₃, with sub-micron grains, could be successfully fabricated using screen-printing method with the novel hybrid sol-gel/nanocrystalline route. Densification studies by other researcher [92] of PZT thick films 10µm thick on alumina substrate indicate that the films have to be sintered to 1150°C to reduce the pores. With the novel technology developed in this thesis, the sintering temperature could be remarkably decreased from 1100 ~1200°C to 800°C.

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Figure 4-8. FE-SEM images for surface morphologies of screen-printing PZT thick films on Au/Al₂O₃ substrate at different sintering temperature for 30 minutes: 650°C (a), 700°C (b), 750°C (c), and 800°C (d).

Figure 4-9. FE-SEM images for cross-section of screen-printing PZT thick films on Au/Al₂O₃ substrate at different sintering temperature for 30 minutes: 650°C (a), 700°C (b), 750°C (c), and 800°C (d).

4.4 Low temperature processing of bulk ceramics

4.4.1 Experiment Process

The PZT53/47 paste consists of nano-sized powder and sol-gel precursor solution for screen-printing was dried into powder at 110°C for 2 hours, after which

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the powders were grounded. The resultant powder was uniaxially pressed into discs under a pressure of 12 tons, followed with pre-heat treatment at 500°C to burn out the organic components. The resultant green bodies were sintered at 650°C ~ 1100°C for 1 hour in closed crucible. PbO and PZT powders were employed to prevent lead loss during sintering. Heating and cooling rates were 600 °C/hour.

4.4.2 Density and porosity of sintered ceramics

The density was determined according to Archimedes' principle: the specimen was saturated with water and weighed in air and in water. The density ρ_{exp} and apparent porosity P_{open} could be calculated from:

$$\rho_{\text{exp}} = \frac{W_D}{W_w - W_f} \cdot \rho_{\text{water}}$$

$$P_{\text{open}} = \frac{W_w - W_D}{W_w - W_f}$$

where

W_w : the wet weight of saturated specimen in air [g];

W_f : the floating weight of saturated specimen immersed in water [g];

W_D : the dry weight of the specimen [g];

ρ_{water} : the density of water [normally 1.0 g/cm³];

P_{open} : the apparent porosity of specimen [%].

According to the molar weight and lattice constant of a cubic perovskite phase PZT53/47, a theoretical density is calculated to be 8.015 g/cm³. Then the relative density could be determined as $\rho_r = \rho_{\text{exp}}/8.015$. The results of ρ_{exp} , ρ_r and P_{open} of PZT ceramics sintered at different temperatures are given in Table 4-1 and Figure 4-10. The density of green body and samples after burning-out, which calculated from the ratio of weight to volume, are also given for comparison.

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It is shown that the as-pressed green body has a relative density up to 62% of the theoretical density. After burning-out at 500°C, it increases to 70%. At the same time, the ceramic samples after sintering show a high density above 98% of theoretical one. Especially, the relative density of specimen sintered at 750°C increases remarkably from 80% to 95% of the sample sintered at 800°C. After that the density increases with increasing sintering temperatures continuously but with a smaller increment. This result corresponds to the grain size changing observed in FE-SEM results, which will be presented in the following section. Moreover, the specimen has an apparent porosity as low as 1% after sintered at 850°C. Such a high density and low porosity should contribute to the improvement of dielectric property and ferroelectric property of specimens.

Thus we can come to the conclusion that dense PZT53/47 ceramic can be obtained by sintering at above 800°C, and this is a relatively low sintering temperature of PZT 53/47 ceramics.

Table 4- 1. Physical properties of PZT ceramic sintered at different temperature.

Samples	As-pressed	After burnout	750 (°C)	800 (°C)	850 (°C)	900 (°C)	950 (°C)	1000 (°C)
$\rho_{\text{exp}} (\text{g}\cdot\text{cm}^{-3})$	4.95	5.62	6.41	7.66	7.82	7.86	7.86	7.92
$\rho_{\text{r}} (\%)$	61.8	70.1	80.0	95.5	97.5	98.0	98.0	98.8
$P_{\text{open}} (\%)$			17.6	2.7	0.8	1.1	0.9	0.9

Figure 4-10. Relative density and apparent porosity of PZT ceramics sintered at different temperatures.

4.4.3 Cross-section and surface morphology of ceramics

PZT ceramics prepared by conventional ceramics process using the high-energy ball milled powder were sintered for comparison purpose. The fracture surface morphology of the ceramic sample sintered at 750 °C for 1 hour is given in Figure 4-11, agglomerate of the as-milled powder is given as well. It is shown that, while the grain has grown after sintering, the ceramic sample is quite porous. It might be ascribed to the low packing density because of the heavily agglomeration of particles. It is generally known that the larger the agglomerate size, the higher is the sintering temperature. During the sintering of an agglomerated powder, smaller inter-crystalline pores (several nanometers) will disappear first, thereby the agglomerate of nano-sized crystallites develop into one grain. Therefore, the widely spaced inter-agglomerate

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pores are the only pores present to pin grain boundaries and control grain growth. Minimizing the agglomerate size of particles is essential to obtain ceramics with high density.

With the hybrid processing developed in this thesis, agglomeration of powders was eliminated and PZT green body with density as large as 70% could be prepared. Figure 4-12 and Figure 4-13 show the fracture and natural surface morphologies of PZT ceramics sintered at different temperatures. Two stages of sintering could be observed from the images.

For those samples sintered at temperature lower than 750°C, grains in ceramic body are in granular shape. The average grain size is 100 nm, increasing gradually with increasing sintering temperature. However, these samples have a porous microstructure, with a low relative density of less than 80%.

The samples sintered above 800°C, the average grain size increases sharply to 600 ~700 nm. The grains developed fully so that a dense microstructure without inter-granular pores is observed. After sintered at 1000°C for 1 hour, density of PZT ceramics almost reach their theoretical value as has been indicated in the last section. On the other hand, while the measured density increases with increasing sintering temperature, no apparent grain growth is observed in the ceramics; and the average angle at grain junctions is around 120°C. This indicates that the grain growth is inhibited at around 850°C.

It is well known that the smaller the particle size of the starting materials is, the easier the secondary recrystallization (exaggerated grain growth) occurs during sintering. It is worth to note that although the starting powders are ball-milled into less than 30 nm, the grain-size distributions in all samples are still within a very narrow range. This means that no secondary recrystallization occurs during sintering. We

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attribute this phenomenon to the uniform size distribution of PZT particles in the pellet. Generally, the final grain size and the temperature required to reach full density are determined by the agglomerate size other than crystallite size. Since the final grain is sub-micron in size and the sintering temperature is not so high, we can come to the conclusion that the agglomerates, if any, are very small in size, or, are eliminated in the paste prepared by the hybrid process. This is one of the important features of this successful process.

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Figure 4-1 1. (a) Cross-section of PZT ceramics sintered at 750°C for 1 hour, prepared by conventional ceramic process using high-energy ball milled powder; (b) agglomerates of nanocrystalline PZT powder after high-energy ball milling.

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Figure 4-12. Fracture morphologies of PZT ceramics sintered at different temperatures for 1 hour: (a) 650°C, (b) 700°C, (c) 750°C, (d) 800°C, (e) 850°C, (f) 900°C, (g) 950°C, and (h) 1000°C.

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Figure 4-13. As sintered surface morphologies of PZT ceramics sintered at different temperatures for 1 hour: (a) 650°C, (b) 700°C, (c) 750°C, (d) 800°C, (e) 850°C, (f) 900°C, (g) 950°C, and (h) 1000°C.

4.4.4 Dielectric and ferroelectric properties of ceramics

Table 4-2 gives the dielectric constant (measured at 1 kHz) of the PZT ceramics sintered at different temperatures. It is shown that the relative dielectric constant almost remain the same with sintering temperature up to 850°C. It increases greatly with the increase of sintering temperatures from 850°C to 950 °C, and shows continuous but not significant increments thereafter. The increase in dielectric constant of the PZT ceramics can be explained in terms of crystalline size variation, which might be smaller than the observed particle size, as well as degree of crystallinity of the samples as a result of increasing sintering temperatures. For ferroelectric ceramic materials, it is well accepted that the coupling effect between grain boundaries constrains the domain reorientation and domain wall mobility [93, 94]. When the grain size increases, this effect will reduce because that the grain boundary fraction is inversely proportional to the grain size. As a result, the dielectric constant increases with the increase of grain size of the ferroelectric ceramics. Yet no significant grain size increase was observed as the sintering temperature is increased from 850°C to 950 °C. This may be due to the poor crystallinity of the sample sintered at 850°C. The poor crystallinity of the sample sintered at 850°C is also evidenced by the P-E hysteresis measurement as will be discussed later in this section.

The representative P-E hysteresis loops for the ceramics sintered at different temperatures for 1 hour are shown in Figure 4-14. The hysteresis loop of the PZT ceramic sintered at 850°C is not well developed. This observation confirms the poor crystallinity of sample sintered at 850°C, which could be the cause of the low dielectric of 850°C sintered PZT ceramic as mentioned above.

As the sintering temperature is increased to 1000°C, the sample exhibits a typical ferroelectric hysteresis loop with a saturated polarization (P_s) of 24.1 $\mu\text{C}/\text{cm}^2$,

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a remnant polarization (P_r) of $14.1\text{ }\mu\text{C}/\text{cm}^2$, and a coercive field (E_c) of about $13.6\text{ kV}/\text{cm}$.

It may be noted that the dielectric and ferroelectric properties of the PZT ceramics fabricated by the hybrid processing technology in this thesis are in close agreement with the widely reported results in literature [93, 95].

Table 4-2. Dielectric properties of PZT ceramics sintered at different temperature.

Firing temperature ($^{\circ}\text{C}$)	750	800	850	900	950	1000
Relative permittivity ϵ_r	797	806	808	895	1200	1232
Relative density $\rho_r\text{ (g}/\text{cm}^3\text{)}$	80.0	95.5	97.5	98.0	98.0	98.8

Figure 4-14. P-E hysteresis loops of PZT ceramics sintered at 850, 900 and 1000°C.

4.5 Merits of the hybrid sol-gel/nanocrystalline-powder processing technology

As mentioned at the beginning of this chapter, the key point of this novel hybrid processing technology is the combination of sol-gel precursors and nano-size particles. A compact composite after the materials forming inherently has three phases: sol-gel precursor, powder and pores. In this section, merits of the low temperature sintering mechanism will be discussed based on these three aspects.

Firstly, the sol-gel derived phase, as crystallite internally between the particles, acts to bind the powder with each other. As the surface hydroxyl groups are always present on the surface of the PZT powder, the polymer species that are formed during hydrolysis and condensation of the precursor are able to react with the hydroxyl groups. Thus there is a strong adherence between the sol-gel component and oxide surfaces on the individual particles in the system. The microstructure of the annealed matrix exhibits the features of concrete: fine crystallites derived from sol-gel precursor makes up of cement, and the PZT powder makes up of gravels. It could be clearly seen that, the initial density of the matrix is much higher than that of ceramic green body with powders only. This is because that the unoccupied space between powders can easily filled by sol-gel precursor, thereby part of it is occupied by sol-gel derived crystallites after sintering. Moreover, since the particles loaded in the matrix are enwrapped with viscous organic sol-gel precursor, they could slide with each other more easily during forming. As a result, high density of the green body could be achieved with the aid of sol-gel precursor.

During the matrix sintering, nucleation initiates from the sol-gel amorphous phase, the nuclei grow up until all the resultant crystallites begin to impinge on one another. Thus the sol-gel derived crystallites are connected to the powders loaded to

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form aggregates. The newly formed grains will further grow up, and the matrix densification will consequently occur with further increasing sintering temperature in the common sense.

Secondly, according to the packing theory of spherical particle, the larger size the particle is, the larger the space exists between them. In other words, a system packing from smaller particles, if the agglomerates have been eliminated, would have a smaller voids. Thus a high capillary driving force will be produced during either the sol-gel precursor infiltrating or material sintering. A small diffusion distance resulting from the nano-sized particles will also be in favor of mass flow for densification. [165]

Moreover, the high-energy ball milled PZT powder possesses a nano-sized particle size and narrow size distribution, both of which facilitate uniform densification at lower sintering temperature. Smaller particles exhibit fast neck growth due to their larger surface energy and requesting less sintering time or a lower sintering temperature to achieve an equivalent degree of sintering. [165] This has been observed in many ceramic systems.

Finally, since the sintering temperature is lower than 1000°C, enhanced sintering by “liquid phase sintering” seems unlikely. However, the surface of the nano-sized powder after high energy ball milling has been demolished, so it is actually not well crystallized, and it is likely that the particles possess many lattice defects on the surface. The enhanced sintering behavior could therefore be attributed to a “defect-activated sintering” mechanism. [78, 165] Since the particle interior is still well crystallized, mass transportation in the grain interior is not necessary, which needs a high temperature. During sintering, the most mobile entities are vacant crystal lattice sites which migrate from the pores into grain boundaries, giving a reverse flow

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of mass into the pores. Therefore, with the increase of surface/volume ratio coming from nano-sized particle loaded, a fast sintering process is resulted.

4.6 Summary and conclusions

In this chapter, a novel hybrid processing method based on the combination of sol-gel precursor and nano-sized powder for low temperature processing has been developed. PZT thick films on alumina substrate deposited by the screen-printing technology and PZT ceramics have been produced. The thermal properties and phase development of the sol-gel precursor, the physical properties, microstructure, dielectric and ferroelectric properties of PZT films and ceramics have been characterized and evaluated. The low temperature sintering mechanism of the hybrid processing method has been briefly discussed. With this novel processing route, high density of green bodies can be achieved; agglomeration between particles can be eliminated; low crystallization temperature can be realized; and sintering temperature to get fully dense ceramic can be reduced substantially.

CHAPTER 5 DEPOSITION OF PZT THICK FILMS ON Pt/Si SUBSTRATE USING NOVEL HYBRID PROCESSING TECHNOLOGY

In Chapter 4, a novel hybrid processing technology which combines the sol-gel process and high-energy ball-milled nano-powder has been successfully developed. Low temperature processing of PZT thick film on alumina substrate deposited by the screen-printing technology and PZT bulk ceramics, both derived from a homogenous matrix of sol-gel precursor and nano-sized powder, have been produced. The thermal properties and phase development of the sol-gel precursor, physical properties and microstructure of PZT thick films and ceramics have been characterized and evaluated. The main results obtained from these researches showed that the combining of sol-gel processing and nano-composite techniques could provide a good processing approach to prepare dense and well crystallized PZT ferroelectric materials, including bulk ceramics and thick films on Au-Al₂O₃ substrate, from nano-sized starting powders at a relative low processing temperature.

In this chapter, this low temperature processing using this hybrid processing technology is applied to PZT thick film on a platinum coated silicon substrate. Figure 5-1 illustrates the flow chart of the hybrid processing technology for the PZT thick film deposition. Sol-gel derived PZT composite coatings in the 5~50 μm thickness range have been tailored to low temperature processing for integration with silicon process technologies.

Chapter 5 Deposition of PZT composite thick films on Pt/Si substrate

The evaluation of composite PZT thick films was carried out with microstructure and dielectric, and ferroelectric properties measurements. These measurements provide valuable information about the effects of different processing parameters during fabrication technique and for the optimization of the process.

Figure 5-1. Flow chart illustrating the hybrid processing technology for PZT thick film deposition.

5.7 *Infroduction*

With the development of silicon micromachining technology, piezoelectric PZT film integrated on silicon wafer has been considered very promising for their potential applications in micro-devices. The thickness of piezoelectric PZT films for micro-devices can be classified into two groups: 0.5~2 μm for microelectronic and thin film MEMS type devices; and 2~50 μm for actuation and ultrasonic. To date, micro-devices using piezoelectric films with geometries of 1 μm^2 to 100 μm^2 are generally based on the thin films and have attracted great interest. However, many potential applications require film thickness of 2~50 μm and geometries of mm^2 to cm^2 . For applications such as ultrasonic transducer and high-force actuator, dense, crack-free, and uniform piezoelectric PZT films on silicon wafers are often required to produce a high output power or a large generative force. However, integrating of piezoelectric PZT thick films on silicon wafer is still a big challenge in this research area.

To date, the films have been prepared principally by the following four methods: thick layers of thin films (e.g. diol-based [96] or HAC-based sol-gel method [52]); thin layers of thick films (e.g. screen printing) [97]; a mixed method of thin films prepared by sol-gel routes and loaded with powder of similar composition [98]; and hydrothermal method [99]. While screen printing is presently the only practical method for thickness larger than 10 μm , but it requires high temperature sintering. The powder loaded sol-gel process has received more attention for its simplicity and producibility. Sayer et al. [98] have reported the thick PZT films coating using a sol-gel based ceramic-ceramic 0-3 composites. In these composites, the powders act to inhibit crack propagation in multilayer deposition; it is thus easy to get crack-free films of up to 60 μm in thickness on platinum-coated silicon and other substrates.

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However, the thick films fabricated by these modified sol-gel process have poor mechanical and electrical properties, which are mainly due to their porous microstructure [100] and the coarse surface on the film [98]. Therefore, preparing thick uniform PZT films with large area by the sol-gel technique at low processing temperature is still challenging.

5.2 Sol-gel derived PZT thin films

PZT53/47 thin films with 1~18 layers have been deposited using xerogel precursor sol-gel solution in different concentrations without powder loaded for comparison. Preparation procedure of xerogel has been specified in Chapter 3. The sol prepared by dissolving PZT xerogel into 2-methoxyethanol (MOE) was clear and did not show the precipitation. To avoid the possible aging effect and its possible influence on the microstructure and electrical properties, fresh sol was always applied for spin-coating or mixed with PZT powder after stabilized for 24 hours.

Figure 5-2 illustrates the X-ray diffraction pattern of PZT thin film derived from 20 wt% xerogel-MOE precursor solution after annealing at 600°C for 30 minutes. This film was translucent and well crystallized with pure perovskite phase. Figure 5-3 shows the cross-section and surface morphology of a PZT thin film with 9 layer coating. After annealing at 640°C, the 6- μm -thick thin film has a dense microstructure. It is shown from the surface morphology image that it consists of fine perovskite grains with granular structure, and their average size was around 100 nm.

A representative polarization hysteresis loop of a PZT thin film with thickness of 1.1 μm (18 layer coating) is shown in Figure 5-4. The measured remnant polarization P_r , the coercive field E_c , the relative permittivity ϵ_r , and dielectric loss D are 22.1 $\mu\text{C}/\text{cm}^2$, 44.7 kV/cm, 951 and 0.02, respectively. However, 1.1 μm is the

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critical thickness for PZT films derived from pure xerogel-MOE precursor solution at this concentration (20 wt %). Beyond this thickness the cracks appear in the film. Therefore, in order to obtain thicker films, the film deposition process has to be modified.

Figure 5-2. XRD pattern of PZT 53/47 thin film annealed at 600°C for 30 min.

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(a)

(b)

Figure 5-3. FE-SEM images of 9 layer coated PZT53/47 thin films annealed at 640°C for 30min: (a) cross-section and (b) surface morphology.

Figure 5-4. P-E hysteresis loop of 18 layer coated (1.1 μm) thick PZT thin film annealed at 600°C for 30 min.

5.3 Preparation of slurry for PZT composite thick film deposition

As discussed in Chapter 4 and mentioned at the beginning of this chapter, the key point of this novel hybrid processing technology is the combination of sol-gel precursors and nano-size particles. Therefore, we believe that the slurry characteristics are very important for good PZT thick films deposition. How to obtain a uniform and stable slurry is a crucial step.

5.3.1 Slurry preparation

5.3.1.1 Consideration of slurry for thick film spin-coating

.Deposition of PZT thick films on Pt/Si substrate was carried out with spin-coating process. Spin-coating process is a simple process for rapidly depositing film onto relatively flat substrates. The action of spinning causes the solution to spread out and leave behind a uniform coating of the chosen material on the surface of the substrate. It has been studied extensively in the past, and much is known about factors that control coating deposition and the thickness. The final coating thickness, h_f , was predicted in terms of several key solution parameters, according to [101].

$$h_f = x \left[\frac{e}{2(1-x)K} \right]^{1/3},$$

where $e = C\sqrt{\omega}$ and $K = \frac{\rho\omega^2}{3\eta}$ are the evaporation and flow constants, and x

is the solid content of the solution, where ω is the rotation rate, ρ is the solution density, η is its viscosity, and C is a proportionality constant that depends on whether airflow above the surface is laminar or turbulent and on the diffusivity of solvent molecule in air. The film thickness can thus be ascribed to

$$h_f = \frac{x}{\sqrt{\omega}} \left[\frac{3\eta C}{2(1-x)\rho} \right]^{1/3}$$

Accordingly, to increase the thickness of green gel film during spin-coating, larger x and η , or smaller ω and ρ are preferred. Among them, for composite PZT films, the solid content x consists of the weight of powder loaded and the PZT inorganic phase crystallized from sol solution. The latter one as well as the viscosity η and the solution density ρ are directly related to concentration of xerogel in sol solution.

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Moreover, as spin-coating of PZT composite thick films is a process followed by pyrolysis and annealing, the solid content of slurry should play an important role in producing films with dense, crack-free and uniform microstructure.

5.3.1.2 Preparation of uniform slurry

Preparation of the uniform slurry for PZT thick film deposition is illustrated in Figure 5-5. High-energy ball milling (Frisch Pulverisette 5 planetary ball milling machine) was employed to obtain the powders with desired particle size and further to uniformly disperse the powders into the PZT sol-gel solution. Commercial PZT powder (APC850) was used as particle source to be loaded in the PZT53/47 xerogel precursor solution in this thesis. The high-energy ball milling process was employed to produce nano-sized PZT particles. Figure 5-6 shows the FE-SEM images of commercial PZT powders and of dry milled PZT powders, respectively. It is shown that the commercial available PZT powder had a wide distribution of grain size and most of them were above 0.5 μm . A small amount of the powder exhibits a spherical morphology while the remainder show irregular morphologies with sharp facets. It does not avail to the sliding between the particles during forming and densifying. After dry milled at 200rpm for 32 hours, the raw powder particles were smashed into a smaller size. The average particle size estimated from the FE-SEM images was about 20 nm, which is much smaller than that of the raw powders, and had a nearly spherical shape. That is one of the reasons that high energy ball milling process was employed to produce nano-sized particle for the slurry preparation.

Firstly, commercially available PZT powders (APC 850) were high-energy ball milled to get the desired particle size. Secondly, a selected dispersant was added into the milled powders and ball milled for another period of time to get the surface modified powders. The PZT sol-gel solution was then added and mixed with the

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surface modified powders by further ball milling. Finally, the resultant uniform slurry was ready for further processing, such as spin coating, tape casting, screen printing, etc. The key point of slurry preparation is to eliminate the particles as agglomeration. Most of the research reports approaching PZT composite film deposition dispersed PZT powder directly into sol-gel solution with ultrasonic agitation methods. In the high energy ball milling, energy is transferred from the flying WC balls to the milled powder particles by collision. The energy provided is strong enough by the large momentum of WC balls to crash the milled ceramic powders into nano-sized particles, which has been confirmed by the above FE-SEM images. On the other hand, the agglomeration of the nano-sized ball-milled powder was more severe. Therefore, the ball-milled powders were agglomerated too heavily to disperse them into the sol gel solution uniformly and directly. This agglomeration should be avoided during the dispersion of PZT powder in sol-gel precursor solution.

However, such agglomerates of particles are generally too strong to be broken down through subsequent shaking or by ultrasonic agitation method. As has been shown above, the adoption of ball milling technique and dispersant are the key point of the novel hybrid process developed in this thesis. The ball milling process, which is a conventional material process and has been widely used, could be controlled by varying the rotation speed, milling time or dry/wet milling, to obtain certain particle size and uniformity of the slurry. On the other hand, the introduction of dispersant has played a key role in breaking the agglomerates and stabilizes the slurry.

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Figure 5-5. Flow chart illustrating the processing sequence for preparing an uniformly dispersed slurry.

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Figure 5-6. FE-SEM images for (a) PZT raw powders and (b) high-energy milled powders (200rpm/32hr).

5.3.2 Disaggregation of loaded PZT powder

Agglomeration is a natural phenomenon for ceramic powders because the London-van der Waals forces acting between the solid particles are always attractive, and it becomes particularly significant for nano- or submicron-sized powder due to their extremely high surface area. Most nanocrystalline particles currently made are not composed simply of individual crystallites or nano-sized particles. Crystallites made by conventional methods, such as ball milling, tend to bond and form larger units termed “agglomerates” or “aggregates”. This is the major factor responsible for the inhomogeneities in ceramic and composite thick film microstructures, which results in reduced reliability as well as poorer microstructure and electrical properties.

Therefore, to prepare uniform and stable slurry ready for film deposition, it is necessary to eliminate or minimize the number and size of the powder agglomerates. There are essentially two issues encountered, namely breaking the agglomerates into separate units, and keeping them separate without reaggregate in the resultant slurry.

Regarding the first one, since such agglomerates are generally too strong to be broken down through conventional method such as ultrasonic agitation, again the high-energy ball milling technique was employed. As has been mentioned before, the energy provided by high energy ball milling is strong enough to crash the milled powders into fine (nano-sized or submicron-sized) particles; obviously it should be strong enough to separate the fine particles from forming agglomerates. Following that, the second issue how to prevent the separated particles from reaggregation and keep them stable in the resultant slurry is more challenging.

Essentially, it is a fact that the surface of the fine-crystalline particles is occupied by functional groups such as hydroxyl groups. Due to the large surface-area-to-volume ratio of fine-crystalline particles, these functional groups lead to the

formation of hard agglomerates as a result of condensation reactions taking place between individual particles. On the other hand, these groups can act as centers of interaction for necessary organic processing aids such as dispersion aids, binders and the like. Accordingly, by modifying the surface states through organic processing aids, the particle interactions can be controlled efficiently. It is the key of the disagglomeration process to stabilize the ceramic slurry against flocculation. Thus the dispersibility of the resulting ceramic products (PZT thick films) can be greatly improved.

It is known that stable dispersion can be created by manipulation of particle's interaction forces either by the pH adjustment, or by using surfactant. Generally, the first one is built on the electrostatic mechanism, whereas the other one is built on the electrosteric mechanism (a combination of electrostatic stabilization mechanism and steric stabilization mechanism). However, while double-layer repulsion is very flexible and easy to modify, it is not strong enough sometimes to stabilize a slurry/suspension. Reasons could be that the particle size is either too large or the particle is too heavy; the particle surface charge is too low or unstable. An alternative way to modify the particle surface is using surfactant. Surfactants are classified as macromolecule dispersant with molecular weight usually less than 1000, and with a polar functional group or groups. Moreover, electrostatic stabilization with pH adjustment was reported as being less effective than electrosteric stabilization with surfactant for ferroelectric powder suspensions [102]. Spontaneous formation of a particle network structure by polarization of ferroelectric particles may induce a phase separation, indicating difficulty of electrostatic stabilization of ferroelectric powders. Another problem with the pH adjustment in solution is the instability of some ferroelectric ceramic powders in certain pH ranges. For example, though the PZT

suspension could be well dispersed at pH below 7, it is still preferred to use a polyelectrolyte to stabilize a PZT aqueous suspension. It is because that when a large number of the lead ions are dissolved in the acidic condition, it will affect not only the sintering behavior but also the electrical properties of the resultant ceramic [103]. Therefore, electrosteric stabilization using surfactant is more effective to disperse fine ferroelectric powders and to increase the solid content of the suspension.

The surfactant used in the process is organic vehicle and diol. The former is a commonly-used binder in screen-printing processing whose main function is to increase the green strength of the compacts by binding the powder particles together. For slurry preparation, it enables the powder agglomerates to be broken down more easily by using the viscous polymer solution not only to transfer significant stresses to the powder agglomerates but also as a lubricant between particles. The latter one, which has a strong interaction with particle surface, is added to give right visco-elastic behaviour in order to break down the agglomerates during the processing.

5.4 Application of hybrid processing technology to composite PZT thick film deposition

5.4.1 Deposition of PZT composite thick films on Pt coated silicon substrate

The overall procedure for PZT composite thick film deposition is illustrated in Figure 5-7. The slurry used for spin-coating was prepared from PZT xerogel-MOE solution loaded with nano-size PZT powder. 10wt% of vehicle was used as dispersant during slurry preparation. The spinning speed was 3000 rpm and the time was 30 seconds. The substrate used was Pt/Ti/SiO₂/Si-(100) wafer. Ti and Pt were employed as buffer layer and bottom electrode, respectively. Thickness of each layer on silicon

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was 500 nm (SiO_2), 150 nm (Ti) and 150 nm (Pt), respectively. Multiple coating then allowed the building up of desired thickness from 5 μm to 20 μm .

Before the PZT composite film deposition, a pure sol-gel layer was deposited on the Pt bottom electrode as a buffer layer to enhance adhesion between PZT thick films and substrate. A final capping layer of pure sol-gel layer containing no powder completed the deposition. A pure sol-gel layer after every 3 composite layers deposition or less can also enhance the internal density through infiltrate into the pores in the bulk of composite thick films.

According to the thermal analysis results in Chapter 4, annealing of PZT composite needs to take place at temperature as high as 600~650°C. Annealing at lower temperature for prolonged periods results in only partial removal of the residual carbides, and contributes the evaporation of lead oxide. In order to maximize the removal of the carbon and to minimize the lead loss, a rapid increase of temperature to 650°C is desirable. However, increasing the temperature directly from room temperature to 650°C is not beneficial since stresses in the film due to the sudden volume change can lead to cracking; and too rapid removal of organics will result in porosity. From the TGA results, a weight loss occurs at 250°C and 425°C. To reduce the stress in the films during processing, a drying step at 250°C and pyrolyzing step at 500°C were chosen. Both of them were carried out on a hotplate. The purpose of these heating steps is to allow the film to densify and pyrolyze at a slower temperature in order to reduce the tendency of cracking. The densification and pyrolysis of the films appeared as a change in the color of the films so visual observation was used to determine the period of time required to complete the heat treatment. Both of the drying and pyrolyzing step were set at 2–3 minutes. After films deposition, the final annealing process was carried in air at 600~700°C for different times.

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Hereafter, for convenient purpose, the composite PZT thick films developed in this thesis are labeled with a batch number containing four digits. For example, 2013, the first two is the weight concentration of PZT xerogel in MOE solution, 20 wt%; the last two is the mass ratio of load PZT powder to PZT xerogel solution, i.e. 1 to 3.

Figure 5-7. Flow chart for spin-coating PZT composite thick film on Pt/Si substrates.

5.4.2 Nano-sized granular grains in the PZT composite thick films

As illustrated in Figure 5-6, the commercial PZT53/47 powder after high-energy ball milling had a nano-sized particle, which is about 20 nm, and all of them had a round shape. After dispersed it into xerogel solution with the help of vehicle used as dispersant, uniform slurries were obtained and spun onto Pt coated silicon substrate. Figure 5-8 shows an FE-SEM micrograph of PZT composite thick films (4011) after annealed at 700°C for 30 minutes. It can be observed that the grains in the composite film have an average size of 30 nm, estimated from the FE-SEM images.

During the drying, pre-heating and annealing processes, with the volatilization and combustion of the organic components as well as the sintering of the inorganic composition, the coated green film will shrink continually. Although this isotropic shrinkage occurred in the bulk body, the shrinkage is limited in the *X*- and *Y*-axis directions in the films due to the restriction by the substrate. To fabricate a dense film, it is essential that the shrinkage in the *Z*-axis direction compensate for shrinkage in the other two directions. In a film derived from slurry with particles loaded, the smaller the particles dispersed, the easier the movement of the particles in the film. And the round shape is preferred for this movement. Therefore, films derived from slurry using nano-sized particles and dispersant are supposed to be not only crack-free but also having a higher density.

Figure 5-8. Granular grains in PZT composite thick films (4011) derived from slurry with nano-sized particles loaded.

5.4.3 Microstructure of PZT thick films derived from slurry with nano-sized particles dispersed

Figure 5-9 shows the cross-section and surface morphology FE-SEM images of PZT thick films derived from the slurry with loaded nano-sized powder particles. The film was deposited in total of 14 layers, consisting of 5 layers of thin film and 9 layers of composite thick films. The total thickness of the film was 10.8 μm . the average thickness for one slurry coating is estimated to be about 1.2 μm .

From the cross-sectional micrograph, it is clearly shown that the resultant PZT composite thick film has uniform and compact microstructure with a high density. Excellent adhesion occurs between the ceramic films and the underlying platinum-

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coated silicon substrate. The nano-sized grains in the film developed fully and connected with one another. The surface is relatively smooth throughout the whole films. No structural aggregation due to the loading of powder particles is observed. This can be ascribed to the successful elimination of the agglomeration of the nano-sized particle in the hybrid process. While micro-cracks are observed in the surface morphology images, none of them penetrated down to the bottom electrode.

There are intrinsically three phases in the PZT composite thick films: powder, sol-gel derived phase, and porosity. The powder loaded builds up the main body of the thick films. The sol-gel derived phase acts to bind the powder phase internally between grains and also to bind the overall coating to the substrate. Since the formation of the sol-gel phase involves the drying and annealing of a solution which has 10~25 wt% solids, substantial shrinkage of this phase is inevitable. Fine particle size, which is in nanometer scale in this novel hybrid process, facilitates particle packing so that dense microstructure could be achieved.

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Figure 5-9. FE-SEM images of PZT thick films (4012) derived from slurry loaded with nano-sized particles. (a) Cross-section; and (b) surface morphology.

5.4.4 Dielectric and ferroelectric properties of the PZT thick films

Figure 5-10 shows the frequency dependence of relative permittivity ϵ_r and dielectric loss D for PZT composite thick films on platinum-coated silicon substrated (4013). The measurement was carried out ranging from 100Hz to 1 MHz at 50 mV using a 4284 precision LCR meter.

The relative permittivity ϵ_r is 1115 and dielectric loss D is 0.009 at 1 kHz. These values are comparable with those of bulk materials (normally about 1300) and thin films ($\epsilon_r = 951$, $D = 0.02$). Because the slurry derived PZT53/47 films is actually a 0-3 composite, with ceramic particles surrounded by sol-gel derived grains, it is reasonable that the resultant thick film has a comparable property with them.

It is generally known that the microstructure and other factors such as grain size, porosity, stress and interfacial effects may be responsible for the lower dielectric constant [27]. Although thickness-dependent properties have been reported for thin layer films, it will not have a significant effect upon tens of microns thick films. Stress is also expected to influence dielectric properties. But to the fine particle loaded 0-3 composite-like film it is another secondary effect. Generally, the main influential factor may be the porosity that originates from organic evaporation and agglomeration. Since the porosity is remarkably decreased and microstructure is dense in films derived from slurry loaded with nano-sized particles, the dielectric properties have substantially improved.

Figure 5-11 shows the ferroelectricity inherent to PZT thick films derived from slurry with nano-sized particle loaded. The remnant polarization P_r and coercive field E_c for composite film 4013 are $11.7 \mu\text{C}/\text{cm}^2$ and 42.3 kV/cm, respectively. Since the coercive field E_c refers to the field value required to reverse the direction of the domain by definition, the increase of E_c indicates that domain reversal in PZT

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composite thick films from nano-sized particles becomes difficult. The relatively lower P_r is ascribable to the poor ferroelectric properties of the high-energy ball milled nano-sized PZT powders.

It is revealed that the combination of the nano particles and sol gel precursor solution is effective in preparing dense, thick film by spin coating. Miniature devices could be produced with such thick films.

Figure 5-10. Frequency dependence of dielectric property at room temperture for PZT composite thick films (4013) derived from nano-sized particle loaded slurry.

Figure 5-11. P-E hysteresis loop of PZT thick films (4013) on Pt/Si substrate derived from slurry with nano-sized particle loaded.

5.5 Optimization of hybrid processing technology in slurry characters

As demonstrated in previous sections, the novel hybrid processing technology developed in this thesis is a combination of the sol-gel process and ball-milling process. Slurry consisting of sol solution and ceramic powder is prepared and spun on silicon substrate to deposit PZT composite thick films. Thus the characteristics of slurry employed should have an important effect on the final composite thick film's microstructure and electrical properties. The slurry characteristics include: xerogel precursor concentration in the sol solution, particle size of the powder loaded in the sol solution, mass ratio of powder to sol solution, and content of dispersant (vehicle) used for powder disaggregation.

5.5.1 Concentration of xerogel solution

From a simplified overview, the slurry for film deposition is constituted of two elements: powder and solution. In other words, the characteristics of the xerogel solution employed for slurry fabrication should have an important effect on the final thick films. Generally speaking, these characteristics include viscosity, solid content, rheological property, density, vapor pressure and acidity, etc.. One of the methods to control the solution characteristics is to vary the xerogel solute content in sol solution. Solution with a higher concentration of xerogel will have a larger viscosity, which will conduce to suspend PZT ceramic powder.

20wt% and 40wt% sol solution were fabricated by dissolving PZT xerogel in MOE. After loaded with fine PZT powder, stable and uniform slurries were obtained and then used to deposit multilayer PZT thick films on silicon substrate. Cross-section microstructures of the films obtained are compared in Figure 5-12.

It is observed from the FE-SEM images that the PZT thick film derived from slurry with a higher xerogel solute concentration in MOE solvent was a denser microstructure. It might be partially due to the higher solid content crystallized from the matrix sol solution, which can fill in the interspaces among the particles loaded. Moreover, the films derived from slurry with higher solution concentration have a larger single coating thickness, namely 0.55 μm for 20wt% and 1.1 μm for 40wt% solution.

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Figure 5-12. Cross-section of PZT thick films derived from slurries with different concentration of precursor solution: (a) 20wt% and (b) 40wt%.

5.5.2 Powder size

Powder is another important component of the slurry for PZT composite thick films deposition. The effect of the powder characteristics (such as powder size) on film properties mainly depends on how it affects the resultant microstructure. Two kinds of powder with different size distribution, micron-sized and nano-sized, were employed for PZT thick films deposition. After multiple coatings, both samples were annealed at 700°C for 30 minutes. Comparison of the cross-sectional microstructure is shown in Figure 5-13. Dielectric and ferroelectric properties of PZT composite thick films with micron-sized and nano-sized powder are summarized in Table 5-1.

It is observed that in the PZT composite thick films derived from slurry with powder loaded, there inherently exist three phases within the microstructure, namely sol-gel derived phase, loaded powder phase and porosity. However, the phase distributions are quite different. The micro-sized powder derived film has porous microstructure and many large size pores, whereas the volume fraction of the pores in nano-sized powder derived films can be ignored.

The difference in microstructure result in the difference in dielectric and ferroelectric properties. As shown in Table 5-1, with the loaded powder size decreasing from micron-size to nano-size, the relative permittivity increased from 530 to 1115, whereas dielectric loss and remnant polarization decreased from 0.018 to 0.009, and $16.0 \mu\text{C}/\text{cm}^2$ to $11.7 \mu\text{C}/\text{cm}^2$, respectively. The difference in electrical properties is believed to be directly related to the microstructure of films.

Barrow et.al. [104] introduced four dielectric constant models for 0-3 composites with two phases. In all cases, the presence of a high permittivity phase increased the overall permittivity values of the composite, and vice versa. In our case, the large number of the pores content, as a low permittivity content, obviously

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reduces the overall dielectric constant of the films. That is why the micro-sized powder derived film has apparently lower permittivity than that of the nano-sized one. As for the ferroelectric properties, we can explain as follows. The primary micron-sized powder is of good ferroelectric properties, while the nano-sized powder has many defects and imperfections that result from high-energy ball milling. Since only the sol-gel phase was processed at the selected process temperature, the crystallinity of the nano-sized powders loaded would not be improved apparently during sintering. That is why the nano-sized powder derived film has relatively lower ferroelectric properties.

Table 5- 1. Electrical properties of PZT thick films with different powder loaded.

PZT films using different powder size		Micron-sized	Nano-sized
Dielectric properties (1 H z)	Relative permittivity ϵ_r	530	1115
	Dielectric loss D	0.018	0.009
Ferroelectric properties	Remnant polarization P_r	$16.0\mu\text{C}/\text{cm}^2$	$11.7\mu\text{C}/\text{cm}^2$
	Coercive filed E_c	44.9 kV/cm	42.3 kV/cm
	Shape of hysteresis loop	Lossy	Sharp

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Figure 5-13. Cross-section of PZT composite thick films derived from slurries with different powder loaded: (a) micron-sized powder, (b) nano-sized powder.

5.5.3 Slurry composition: mass ratio of powder to solution

Since xerogel solution and PZT powder are the most two important components of the slurry for PZT composite thick film deposition, the mass ratio of PZT powder to solution (p/s) should be an important characteristic of the slurry. In a composite film coated on a substrate, when there is sufficient solution around, i.e., a lower powder solution ratio, most of the PZT particles are fully coated and bound together by the matrix; and voids between the particles are filled with sol derived phase. Whereas too low the powder solution ratio does not help to get uniform and thick single coating films. When there is insufficient matrix available, i.e. too high the powder solution ratio, some of the PZT particles or surface cannot be coated with the binder, and the space between the particles is filled with air instead of the sol derived phase. This results in increased porosity and decreased density. Moreover, a too high powder solution ratio in the slurry induces too high viscosity of the slurry. This kind of slurry is not suitable for spin-coating because of its poor fluidity, and it is not beneficial to obtain a uniform microstructure. Thus the powder solution ratio should have an optimum value.

Figure 5-14 shows the cross-section of PZT composite thick films derived from slurries with different powder solution ratios. It is clearly shown in the images that the single layer coating thicknesses increase with increasing powder solution ratio (i.e. p/s , p is the weight of powder loaded; s is the weight of xerogel solution). Figure 5-15 illustrates the dependence of single layer coating thickness on p/s . The endnotes “ n ” and “ s ” after the batch number represent that this film is derived from slurry loaded with nano-sized and submicron-sized powder, respectively. It is found that the average single layer coating thickness is determined by the solution concentration, powder size, powder solution ratio. Among them, the average single layer coating

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thickness is mainly determined by the solution concentration. It increases with the increase of solution concentration. For PZT composite thick film derived from the same concentration of solution, a perfect linear relationship is observed between the single layer coating thickness and the powder solution mass ratio within the investigation range. In addition, PZT composite thick films derived from slurry loaded with nano-size powder has a larger single coating thickness than those with submicron-sized powder.

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Figure 5-14. FE-SEM image for cross-section of PZT thick films with different power solution ratio: (a) 4013n, (b) 4012n.

Figure 5-15. Dependence of single layer coating thickness on powder solution ratio.

5.5.4 Vehicle content

As discussed in previous sections, because of high surface energy of PZT powder after ball milling, the fine size powders were agglomerated heavily so that it is difficult to disperse them into the matrix sol gel solution. Thus, organic vehicle is employed as dispersant to perform surface modification of the PZT powder so as to obtain uniform and stable slurry for PZT composite thick films deposition. Moreover, the organic vehicle used also acts as a lubricant between powder particles during slurry preparation.

Three different fractions of the vehicle, 10 wt%, 8 wt%, and 5 wt%, were introduced into the PZT powder for surface modification by the ball-milling method. Features of the powder obtained are given in Table 5-2. Corresponding slurries for film deposition were prepared by dispersing them in 20 wt% MOE-based xerogel

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solution at a powder solution mass ratio of 1: 2. PZT thick films were then spin-coated on silicon substrate and annealed in air.

Figure 5-16 shows the cross-section of PZT thick films derived from slurries with different contents of vehicle added. It might be concluded that under same conditions, the lower vehicle content, the denser the microstructure of final films. However, too low a vehicle content might not be able to fully enwrap the particles so that it can not eliminate the agglomerates of powder. An appropriate content of vehicle is required to exert an optimized effect on the elimination of agglomeration.

Dielectric and ferroelectric properties of the PZT composite thick films using 5wt% and 8wt% vehicle are given in Figure 5-17 and Figure 5-18, respectively. It is revealed that the relative permittivity of the films increases with decreasing vehicle content. It may be ascribed to the change in film microstructure, lower porosity, with the vehicle content changes. The remnant and saturation polarization increases with the decrease of vehicle content as well.

Table 5-2. PZT powders with different vehicle content added.

Vehicle content	5 wt%	8 wt%	10wt%
Feature of the powder after surface modifying	Dry powder, the particles segregated from one another, good fluidity	Particles bound together, clay-like	Paste-like

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Figure 5-16 (continued). Cross-section of PZT thick films (2012) derived from slurries with different vehicle content, annealed at 700°C/30 min: (a) 5wt%, (b) 8wt% and (c) 10wt%.

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Figure 5-16. Cross-section of PZT thick films (2012) derived from slurries with different vehicle content, annealed at 700°C/30 min: (a) 5wt%, (b) 8wt% and (c) 10wt%.

Figure 5-17. Dielectric properties of PZT thick films (2012) derived fi-om slurries with different vehicle content (5wt% and 8wt%).

Figure 5-18. P-E hysteresis loop of PZT thick films (2012) with 5wt% and 8wt% vehicle added and annealed at 650 °C for 30 min.

5.6 Optimization of hybrid processing technology in process

One of the features of the novel hybrid processing technology developed in this thesis is the introduction of fine size powder loaded in slurry for PZT composite thick film deposition. It is essential to obtain crack-free PZT thick films with uniform and dense microstructure. Advantages of the microstructure include good mechanical toughness because of effective crack inhibition at the interface between the powder grains, and good mechanical/electrical inter-particle coupling because of similar or complementary electrical properties between the powder and the sol-gel derived phase.

However, although P-E hysteresis loops of the PZT thick films with such nano-sized grains could be obtained (Figure 5-11), it is slim and the P_r is relatively small in comparison with the pure thin film with the same composition (see Figure 5-4). The average grain size of the PZT composite thick film after annealing is about 30 nm, which was smaller than that of 100 nm in thin film. Since ferroelectricity is a long-order phenomenon, the nano-sized grains in films should be part of the origin of the weak ferroelectricity. In addition, the poor ferroelectric properties can also be attributed to the defects and imperfections on the surface of the grains, which is inherent from the high-energy ball milled nano-powders. Therefore, optimizing the particle/grain size of the powder phase is necessary to balance the ferroelectric properties and the microstructure uniformity.

5.6.1 Annealing of PZT composite thick films

5.6.1.1 Effect of annealing temperature on electric properties

Fine particle size is essential to obtain a PZT composite thick film with uniform and dense microstructure. It is well known that the electric properties of the ferroelectric films is generally dependent on microstructure properties and influenced

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by the various factors such as grain size, grain boundary, crystallinity, and dipole orientation [27]. Moreover, because the size effect is a well-known phenomenon in ferroelectric materials, large grain size is preferred in ferroelectric materials to achieve required properties. High temperature annealing is generally used to obtain good electric properties of ferroelectric materials.

According to the annealing temperature dependence on electric properties, as illustrated in Figure 5-17 and Figure 5-19, both the relative permittivity, ϵ_r , and remnant polarization, P_r , increase with increasing annealing temperature. It can be explained in terms of grain size variation as well as degree of crystallinity of the films as a result of the increase of annealing temperature. Because this annealing temperature of 650°C is not a temperature where solid state diffusion between the phase occurs, the PZT composite thick films is not sintered indeed. It is reasonable that there is no obvious increase of grain size observed in FE-SEM images. Therefore, we could ascribe the variation of the electric properties mainly to the change of crystallinity and it is evident from the dielectric loss and I-V characteristic investigations in addition.

Figure 5-20 and Figure 5-21 show the annealing temperature dependence of dielectric loss and I-V characteristics of PZT composite thick films. With the annealing temperature increases, both dielectric loss and leakage current decreased correspondingly. The dielectric loss is related to energy dissipation in the films. Usually, for frequencies below 10^{10} Hz, the dielectric loss is attributed to two mechanisms: relaxation loss and resistive loss [27]. In the case of the relaxation loss mechanism, it is the relaxation of the dipole or ionic transfer, which dissipates the energy. In the resistive loss mechanism, the energy is consumed by mobile charges in the film, which give rise to a leakage current. In the case of ac level of 50 mV at 1

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kHz, the resistive loss is small. Therefore the relaxation loss would be the dominant mechanism. The lower dielectric loss and leakage current indicates lower defects or imperfections in the films.

Figure 5-19. P-E hysteresis loop of PZT thick films with 5wt% vehicle added and annealed at 650°C and 650°C for 30 min, respectively.

Figure 5-20. Annealing temperature dependence of dielectric loss.

Figure 5-21. I-V characteristic versus annealing temperature of PZT thick films.

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5.6.1.2 High temperature annealing of PZT composite thick films on Pt/Ti/SiO₂ substrate

Although ferroelectric hysteresis loops could be obtained, as shown in Figure 5-19, they are relatively slim. And the value of the remnant polarization P_r is quite small in comparison with that of the bulk ceramics with the same composition. Therefore it is essential to increase the grain size from nanometer to sub-micron meter. High temperature annealing was employed further to 850°C to obtain sufficient grain size.

Figure 5-22 shows the cross-section of PZT composite thick films on platinum coated silicon substrates. The annealing temperature is altered between 700°C and 850°C for 1 or 2 hours. It is shown that the particles have grown to a certain extent during annealing, but it is not remarkably. Although some large size texture is observed in the film annealed at 850°C, the grains still remains a granular shape. This result is different from the sintering research of bulk ceramics and screen-printed thick films using the same hybrid technology, where the final submicron-sized grains were fully developed at 800°C. This was probably because that the Pt-coated silicon substrate constrained the densification of the PZT composite thick films, a high porosity was inherited in the films. And since the films had very small grains in the materials and the grains are in contact with vapor phase, the surface diffusion rounded off the grains to achieve the dihedral angle (etching effect).

On the other hand, high temperature annealing would seriously damage the bottom electrode. It is observed in Figure 5-23 that the films annealed at temperature higher than 700°C were peeled off from the underlying Pt/Ti layer. Cracks occurred at the top surface of arched films. It is difficult to measure the electrical properties of PZT films due to the peeling of the platinum bottom electrode. It is generally accepted

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that Pt/Ti coated silicon wafer cannot withstand high temperature annealing because of diffusion and oxidation of the titanium adhesion layer and the release of stress of the bottom electrode made by sputtering. The stresses developed due to oxidation of Ti to TiO_2 are released by the separation of the lower section of the Pt layer into ellipsoidal islands, in contrast to the formation of protrusion on the Pt surface [105]. It is clearly undesirable since it undermines the adhesion of the Pt/Ti electrode. Generally, as shown in Figure 5-24, 650°C is the highest annealing temperature for PZT composite thick films on Pt/Ti/ SiO_2 /Si substrate without peeling off.

Figure 5-22 (continued). FE-SEM images for the cross-section of PZT53/47 4013 thick films annealed at: (a) 700°C/1hr, (b) 750°C/2hr, (c) 800°C/1hr, (d) 800°C/2hr, and (e) 850°C/1hr.

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Figure 5-22 (continued). FE-SEM images for the cross-section of PZT53/47 4013 thick films annealed at: (a) 700°C/1hr, (b) 750°C/2hr, (c) 800°C/1hr, (d) 800°C/2hr, and (e) 850°C/1hr.

Figure 5-22. FE-SEM images for the cross-section of PZT53/47 4013 thick films annealed at: (a) 700°C/1hr, (b) 750°C/2hr, (c) 800°C/1hr, (d) 800°C/2hr, and (e) 850°C/1hr.

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Figure 5-23. FE-SEM images of PZT thick films annealed at high temperature: (a) 2011, 700°C/1hr, (b) 4013, 850°C/1hr. Bottom electrodes are peeled off from substrate, and cracks occurred at the top surface of film.

Figure 5-24. PZT composite thick films (3023) annealed at 650°C for 30 minutes. The laminated structure of Pt/Ti/SiO₂ is observed without blistering.

5.6.1.3 High temperature annealing of PZT thick films on Pt/TiO₂/SiO₂ substrate

For purpose of integration with silicon processing, PZT films have to be deposited on platinum coated silicon wafer. Platinum has thus been adopted as the standard electrode material for PZT films to silicon substrate. Various researchers have examined the interactions between the Pt electrode and adhesion layers. Platinum was originally chosen as a bottom electrode layer because it does not oxidize and remains conductive after the PZT deposition process and post-deposition heat treatments [106]. However, its adhesion to SiO₂ is poor; therefore, titanium was chosen as an adhesion layer between the Pt bottom electrode and the underlying films primarily because it is known to adhere well to most oxides. The titanium layer also

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inhibits interdiffusion between the Si and Pt films, preventing the formation of adhesion killing-platinum silicides [107]. However during experiments, it has been reported that titanium diffuses from the adhesion layer into the grain boundaries of the platinum film and oxidizes or forms PtTi phases during the annealing cycles used in *ex situ* processing methods to form the perovskite phase [107, 108].

Various solutions to the Ti problem were attempted, including oxidizing the surface of the titanium film to form a TiO₂ layer prior to the deposition of the Pt film [109], or replacing the titanium adhesion layer with TiN [108], TiO₂ [110], Zr [111], or Ta [110, 111]. The deposition of a stable TiO₂ layer and a high-temperature Pt deposition was found to limit titanium diffusion and oxidation [108], while the TiN adhesion layer prevented Ti diffusion into the Pt grain boundaries, but oxidized during subsequent processing. Zr and Ta adhesion layers were found to oxidize during the heat treatments without diffusing into the Pt. Therefore, TiO₂ was chosen as the adhesion layer between Platinum layer and silicon substrate.

After TiO₂ and Pt were deposited on the silicon wafer by sputtering, PZT composite thick films were then spin-coated and annealed at 700°C to 800°C for 1 hour. Figure 5-25 shows one of the cross-sections of PZT composite thick films (3025) that annealed at 800°C for one hour. It is clearly shown that with TiO₂ as adhesion layer instead of Ti, there is no peeling observed in the Pt bottom electrode.

Dependence of dielectric properties on annealing temperature is given in Figure 5-26. It is clearly shown that with increasing annealing temperature the relative permittivity increases remarkably, which could be ascribed to the increase of grain size and crystallinity. Dielectric loss increased at high annealing temperature. It is due to the high lead loss at high temperature treatment, where high concentration of vacancies is induced.

Figure 5-27 shows the polarization hysteresis loops of PZT thick films measured at room temperature as a function of annealing temperature. The values of remnant polarization P_r , saturation polarization P_s , and coercive field determined from the hysteresis loops are plotted in Figure 5-28. With increasing annealing temperature, larger remnant polarization, saturation polarization, and lower coercive fields were shown. The sharpest hysteresis loop was observed at 800°C. From the above observation, one may conclude that the crystallinity in films annealed at 800°C is most developed.

From the hysteresis loops, the ferroelectric polarization and coercive fields were determined. The evolution of ferroelectric polarization values and coercive fields were measured under various applied electric field for films annealing at 800 °C. As shown in Figure 5-29, the evolution of polarization and coercive field with applied field shows a slope change at a saturation field of approximately 250 V.

Even so, the ferroelectric hysteresis loop is still quite slim, and the remnant polarization is relatively small. The ferroelectric properties of the PZT composite thick films derived from fine size powder are inferior to those of the bulk materials.

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Figure 5-25. Cross-section of PZT thick films (3025) on Pt/TiO₂/SiO₂/Si substrate after annealing at 800°C for 1hr. No blistering observed.

Figure 5-26. Dielectric properties of PZT thick films on Pt/TiO₂ coated Si.

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Figure 5-27. P-E hysteresis loops of PZT thick films on Pt/TiO₂/Si and annealed at various temperatures.

Figure 5-28. The saturation and remnant polarization (P_s and P_r), and coercive field (E_c) of PZT thick films on Pt/TiO₂/Si annealed at various temperature.

Figure 5-29. Evolution of polarization and coercive field with applied field for PZT thick films annealed at 800°C.

5.6.2 Loaded PZT powder

Although the use of the nano-sized powder is of great benefit to the uniformity of the microstructure, selection of the powder size in the proposed composite route has to be undertaken with care since we have to compromise between uniformity of the microstructure and a heat-treatment temperature that generates good ferroelectric properties within the powder. This is because of not only the uniformity of the microstructure, but also the properties of the powder itself largely contribute to the overall properties of the thick films. This should also be followed during a milling schedule so as to reduce the particle size range without appreciably compromising piezoelectric properties. Therefore, optimization of the particle size or particle

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characteristics loaded in the slurry for thick film deposition may be necessary to balance the particle in slurry and grain in resultant materials, which is directly related to the ferroelectric/piezoelectric properties.

5.6.2.1 Introduction of submicron sized particle

According to our previous experimental results, although the hybrid sol-gel process can produce piezoelectric/ferroelectric films in thickness of about tens of microns, filling the thickness gap between thin film and bulk wafer, the ferroelectric properties have not met the desired requirements for device applications.

Based on the above consideration, submicron-sized PZT powder which was in order of 200 nm ~ 500 nm was mixed with PZT sol solution. After deposited on Pt/Si substrate by spin-coating method, the PZT composite thick films were annealed at 650°C for 30 min.

Figure 5-30 shows FE-SEM images of the cross-section of the resultant PZT composite thick films. It is shown that all the PZT composite thick film derived from slurry loaded with submicron-sized powder have a relative dense and uniform microstructure, although it is a bit coarse in comparison with that of loaded with nano-sized powders. With optimized xerogel solution and powder solution ratio, a comparable microstructure could be achieved. Moreover, as shown in Figure 5-31, the as-sintered surface is reasonably smooth so that it is not necessary to polish it prior to device application.

Moreover, as shown in Figure 5-30 (b), there are two kinds of grains observed in the films. One has an irregular shape and a larger grain size on the order of 300–600 nm; another kind of grain is granular and in a smaller grain size about 50 nm. The large grain might originate from the particle loaded in slurry, and the small one might crystallize and grow from the xerogel solution. Thus a composite island

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structure formed where the larger grains were surrounded by the smaller grains. This kind of microstructure will meet the requirement of both mechanical and electrical properties.

Ferroelectric hysteresis loops shown in Figure 5-32 indicate that the PZT composite thick films derived from slurry loaded with submicron-sized powder exhibit a comparative ferroelectric properties. The remnant polarization P_r is about 20 $\mu\text{C}/\text{cm}^2$. It is much higher than that of thick film using nano-sized powder and is comparable with that of bulk materials.

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Figure 5-30. Cross-section of PZT composite thick film derived from slurry using submicron-sized powders: (a) dense and uniform microstructure in the films and (b) composite structure observed in the films.

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Figure 5-31. Surface morphology of PZT composite thick film derived from slurry using submicron-sized powders.

Figure 5-32. P-E hysteresis loops of PZT composite thick films derived from slurries loaded with submicron-sized and nano-sized powder.

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5.6.2.2 Pre-heat treatment of PZT powder at high temperature

It should be pointed out that the loaded powder in composite films discussed above was not pre-heat treated. The loaded powder phase acted only to enhance the crystallization of the amorphous sol-gel phase and no solid diffusion between the phases occurs. To further optimize the electrical properties of the PZT composite films, the crystallinity of the powder loaded was improved by preheat treating of the PZT powder at high temperature. In other words, development of domain structure in the particles makes sure the PZT thick films have good piezoelectric property.

The PZT powder was press into disc and sintered at 1200°C for 1 hour. After the heat treatment, PZT ceramic disc was crushed and milled for 20 hours to obtain a nano-sized distribution. Figure 5-33 and Figure 5-34 show the dielectric and ferroelectric properties.

Figure 5-33. Dielectric properties of PZT thick films derived from slurries using pre-sintered powders.

Figure 5-34. P-E hysteresis loops of PZT thick films derived from slurries using pre-sintered powders.

5.6.3 Back filling using pure sol-gel layer

To patch up the porosity or rough surface caused by the loaded powder particle, a few layers of the same sol-gel precursor solution (without powder loaded) that was used in the composite slurry were deposited alternately between the composite thick films. For the same reason, the thin film coated before thick films deposition can also increase the adhesion of PZT films with platinum-coated silicon substrate. Figure 5-35 shows the surface morphology and cross-section of the PZT composite thick films with back filling of the pure sol-gel layer. It could be observed that both surface uniformity and inner density have been improved by this method. The reason for this process is attributed to the residual pores in the film originated from flock in the agglomerated particles and decomposition of the carbon content. Therefore, these pores could be infiltrated with the precursor solution to increase the

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film density. The FE-SEM results shows that back filling of pure sol-gel layers is an effective process to improve the film density and surface uniformity.

Figure 5-35. Surface morphology of PZT thick films (4013) after back filling with pure sol-gel solution.

5.6.4 Application of CIP technique

Because the pure sol-gel coating for back filling is still a liquid organic solution, it decomposes and thus shrinks during heat treatment. Thus it could not infiltrate the pores fully in the PZT composite films.

Moreover, during the crystallization of the sol in the slurry, the sol changed to a wet gel and then a dry gel, and finally decomposed to crystallize. These changes to harder matter caused the bridging of the PZT powder and prevented free movement that could make the film dense. Therefore, neither the loaded powder could move to minimize the space nor the PZT phase crystallized from the sol could fill the space.

Cold Isostatic Processing (CIP) is one of the effective methods suitable for producing components with complex geometry; it involves the application of pressure equally to the powder from all sides. This essentially gives a more uniform green density.

To improve the quality of the thick film derived from composite slurry, cold isostatic pressure processing (CIP) has been introduced into the process during thick film deposition. The multilayer green body of PZT thick films after deposition and baking were compressed by applying cold isostatic pressure of 3000 bar for 15 minutes before the final firing. Samples were sealed in a vinyl glove to prevent from the pollution of oil. After CIP processing, samples were fired at 600°C or 650°C for 1 hour.

The following FE-SEM images, Figure 5-36, give the cross-section of PZT composite multilayer films after CIP processed. For the thick films derived with nano-sized particles, samples with CIP process employed are improved in various degrees. Compared with those samples without CIP technique employed, the decrease of film thickness was about 0.5 μm . In other words, it changes about 8% in total for a film of

6-7 μm thickness. The microstructure of samples after CIP processing was also a little denser than those without CIP processing. In comparison with nano-size loaded composite films, however, the CIP process has little impact on either the microstructure, or the electrical properties (as shown in Figure 5-37).

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Figure 5-36. Cross-section of PZT thick films annealed at 650 °C/30min. (a) without CIP and r (b) with CIP processing at 3000 ba.

Figure 5-37, P-E hysteresis loops of PZT thick films annealed at 650°C/30 min.

5.7 Summary and conclusions

A novel hybrid process technology has been successfully developed in this thesis research and applied to PZT composite thick films deposition. This process of composite coatings successfully bridges the technology gap between thin film of ~ 1 μm and bulk ceramic wafer > 50 μm thick. By suspending PZT powder in a PZT sol gel solution, a slurry is made that can be used to coat PZT thick films on a smooth substrate surface. Multiple coatings are required to build up the thickness of the ceramic. Crystallization of the sol gel results in a ceramic-ceramic 0-3 composite material of PZT powder in a PZT sol gel matrix. Due to the similarities between the two materials, the field distribution should be more uniform than a heterogeneous composite. The two phases have good adhesion and allow for even mechanical coupling within the coating.

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A primary aspect of this process is the combination of nanocrystalline particles and a related organo-metallic precursor to produce a dense, nanocrystalline composite. A key phenomenon of the disclosed process is the reactivity of the surface function groups on the crystallite surface with species in sol-gel precursor. This reactivity allows sol-gel thin films to strongly bond to surfaces of the individual crystallites. Upon completion of the reaction, the driving force of agglomeration among the nanocrystalline particles is controlled or reduced.

On the other hand, the functional groups can also give rise to the introduction of dispersant/surfactant to disagglomeration of the loaded powders. Thus the fine size particles could be uniformly dispersed in the framework of the gels after gel-forming reactions of the precursor are completed. The fine size particles in the green bodies are not agglomerates but individual crystallites.

Moreover, the homogeneity of the green film results from not only the elimination of the agglomerates but also the greater ease with which the particles can slide against one another and rearrange without external pressure in the wet gel state.

Another advantage of the novel hybrid process is attributed to utilization of fine size particle in the process. In ordinary compaction of powders, the smaller the powder particle, the smaller the inter-particle pores. Thus, the pore size and porosity in fine size loaded composite films is much smaller than those utilizing micron-sized powders, giving relatively lower permeability and high density in the green bodies.

As a conventional sol gel, coatings with the slurry contain a large amount of residual carbon after drying. The interface between the powder and the sol gel allows more carbon to escape during firing, however, the volume shrinkage from the volatilization of the organics between the powders causes porosity. To reduce the porosity and thus increase the density of the resultant composite films, the slurry

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characteristics, including sol solution concentration, powder size, and powder solution mass ratio, should be chosen with specific purpose.

While fine size powder is essential to obtain a dense and uniform microstructure, it is not good for the materials to achieve required dielectric or ferro/piezoelectric properties. Higher temperature heat treatment could improve the electrical properties by increased grain size and crystallinity of thick films.

There are two main factors to be taken into account when considering the sintering behavior of thick films, compared to bulk components. Firstly, the ratio of surface area to volume of material is much higher in thick film form, exposing a greater fraction of the material to the sintering atmosphere. It is regarded as the reason that induces the granular grain in the composite thick films. Secondly, films are invariably deposited and sintered on a rigid substrate, which results in a large constraint on the sintering shrinkage which would be allowed if the film was free to move. This requires a strong adherence of the film to the material beneath, and a mechanism whereby the anisotropic sintering stresses can transform the shrinkage into a single direction. Under a high annealing temperature, platinum bottom electrode would be peeled off from silicon substrate if the adhesion layer is not strong enough. Replacing Ti by TiO_2 as adhesion layer is an effective approach to prevent the peeling under high temperature annealing.

In addition to high temperature annealing, optimizing the loaded powder with submicron size or pre-heat treatment of powder at high temperature could produce larger grain size in films and increase the degree of crystallinity of the powder.

Back filling the composite thick film with pure sol gel solution without powder loaded and application of cold isostatic pressing technique could also improve the microstructure and thus electrical properties of the PZT composite thick films.

CHAPTER 6 PZT BASED MEMS

PIEZOELECTRIC ULTRASONIC

TRANSDUCERS

MEMS type piezoelectric micromachined ultrasonic transducers (p-MUT) are miniaturized silicon-micromachined acoustic devices. Lead zirconate titanate (PZT) films have shown to be the promising materials for micro-acoustic device applications because of their high electro-mechanical coupling coefficients and excellent piezoelectric actuation.

In this thesis research, piezoelectric ultrasonic diaphragms and phased array with PZT53/47 thick films on silicon wafer have been successfully fabricated using the bulk micromachining technology. This chapter presents the microfabrication and characterization of these devices. Integration of piezoelectric materials and micromachining technologies into MEMS type piezoelectric devices are reviewed at the beginning. The second part presents the design, process development and characteristics of square p-MUT diaphragms. PZT piezoelectric film was deposited onto Pt/Ti//LTO/Si₃N₄/SiO₂/Si substrate by the novel hybrid sol-gel processing technique described in chapter 5. The silicon substrate was wet-etched to obtain a membrane structure. The actuation properties, including deflection amplitude, frequency response and acoustic transmission characteristic are investigated for diaphragms with different dimensions. At last an ultrasonic array as loudspeaker in audio beam application was designed and realized.

6.1 Introduction

As reviewed in Chapter 2, microelectromechanical systems (MEMS) are currently viewed as providing enormous opportunities for perceiving and controlling a variety of physical environments. Three general themes are commonly explored in MEMS: miniaturization, multiplicity, and microelectronics. Numerous MEMS devices forming sensors, actuators, and micro-optical components have been demonstrated based on a wide variety of physical operating principles.

Piezoelectric MEMS are usually operated in one of two modes: sensor or actuator. When used as an actuator, a voltage is applied across a set of electrodes thereby inducing a strain or deformation of the film. This controlled deformation is used to do work. When used as a sensor one usually detects a change in internal dipole moment within the piezoelectric film induced through either a stress or strain. This change in internal dipole moment is usually detected in the form of a charge or voltage developed across a set of appropriately located electrodes surrounding the piezoelectric film.

Bending mode, in which a layer of piezoelectric film is supported by a thin silicon structure membrane, is one of the most popular designs for piezoelectric MEMS devices and has been widely used in cantilever-type accelerometers [112], force sensors [113], diaphragm-type acoustic sensors [114], microvalves and micropumps [115]. The d_{31} mode has to be employed for bending devices using PZT films deposited on Pt-coated silicon substrates because the polarization can only be realized through the film thickness, but the generated displacement to be used, or the applied stress to be detected, is in the film plane [116].

For example, bulk-micromachined MEMS piezoelectric cantilever oscillators that function as microphones and microspeakers have been made using ZnO thin films

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by Lee and White [117, 118]. These devices, with minor modifications, also serve as voltage-to-frequency converters since the device resonant frequency is sensitive to an applied voltage. Micromachined cantilever structures employing piezoelectrics has been fabricated and tested as accelerometers. Acceleration normal to the cantilever plane produces a time-varying stress in the piezoelectric material, which in turn produces a charge which can be detected [119]. Several researchers have fabricated such devices using ZnO thin films [120, 121], and Polla, et al, made a PZT/SiN cantilever accelerometer that is envisioned for implantable pacemaker applications. It senses low frequency vibrations in a pacemaker recipient, thereby monitoring the person's activity level. Based on the activity level, the appropriate electrical stimulus is then sent to the heart.

Polla's group has also fabricated PZT membrane structures that function as pressure sensors and also as audible and ultrasonic acoustic sensors [115, 122]. Impinging acoustic energy or pressure differentials generate stress in the membrane, producing detectable charge on the piezoelectric. One potential application is hearing aids, and the pressure sensors have worked for acoustic emission sensing of microcrack formation in airplane components.

There has been recent interest in the development ultrasonic transducers that are fabricated by the micromachining processes. This has been stimulated in part by requirement for efficient generation and detection of ultrasound in air, where there are many approaches to the problem [123]. One method that does not rely on micromachining is the use of piezoelectric composites, where the electrical and mechanical properties are optimized for generation and reception separately, and a pair of transducers is used for non-contact material inspection, usually with an impedance matching layer [124, 125].

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Thin diaphragms or membranes actuated by piezoelectric films are of interest for ultrasonic transducers and actuators. Standing deflection waves, traveling waves or Lamb waves have been explored for micromotors and micropumps. Other acoustic applications have also been investigated. Ultrasonic transducers have been used in many fields such as underwater acoustic, medical image and nondestructive evaluation, etc.. As the absorption of ultrasound in air is in proportion to square of frequency, it is useful to develop low frequency transducer to cater for in-air acoustic applications, e.g. audio beam loudspeaker.

The first demonstrations of such thin-film devices have been realized with the piezoelectric material ZnO. In the past years much effort has been expended to integrate the ferroelectric material PZT ($\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$) on silicon devices. As known from bulk ceramics, PZT is one of the best piezoelectric materials found to date, and is used in various sensor, actuator, and transducer application [126]. Its relevant piezoelectric coefficients are an orders of magnitude larger than ZnO.

While PZT thick films deposition is a complex research area, integration of piezoelectric PZT layer into MEMS devices poses another challenge. The process of incorporating an active piezoelectric layer between two electrode layers on top a structural layer introduces several materials related problems. Among these are the interaction between the PZT layer and the electrodes, and the effect of the interaction on the piezoelectric properties and adhesion between the two dissimilar materials Pt and PZT. During recent years much progress has been made in this area. The main impetus for its integration into silicon is the prospect of non-volatile, radiation-robust memories. While the early work on PZT thin-film actuators [127] still suffered from integration problems, more recently a number of devices have successfully been fabricated and characterized. Among the piezoelectric devices, these include

cantilever actuators [128, 129], probes for atomic force microscopy [130], ultrasonic micromotors [131, 132], micropumps [133], ultrasonic transducers for medical applications [114], and linear actuators [134].

6.2 Bulk-micromachined MEMS type piezoelectric diaphragm

Due to their intrinsic electromechanical coupling behaviors, piezoelectric materials have been widely used to make actuators and sensors used in smart structures and in MEMS [135-136]. The structure of actuators or sensors in general is constructed mainly by multi-layer diaphragm (or film) with piezoelectric layer embedded in it and its support, the substrate. The multi-layer PZT diaphragms play the function as a mechanical-electrical converter. They convert values of mechanical quantities (deformation, stress, velocity, acceleration, etc.) into suitable electrical signals as being utilized as sensors; whereas the converse effect, as being designated as actuators, are associated with the mechanical movement generated by the application of electrical field. So the properties of the multi-layer PZT diaphragm are the basic parameters in devices design and fabrication.

6.2.1 Design of the diaphragm: devices structure and operation

The structure of the micromachined piezoelectric thin film diaphragm and its cross section sketch is shown Figure 6-1. The main structural components of the membrane are: (100)-oriented silicon, low stress silicon dioxide, and amorphous LPCVD silicon nitride. Low-temperature-oxide (LTO) is superimposed upon it as an adhesion and structure layer. A conducting bottom electrode, Pt/Ti, forms the next layer, and defines the functional area of diaphragm. A PZT thick film was deposited on Pt/Ti/LTO/Si₃N₄/SiO₂/Si wafer as the active layer. The uppermost layer is Pt/Ti top electrode with a layer of polyimide intervenes. The backside silicon was wet

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etched off till the SiO₂ layer. Therefore, the diaphragm is actually a square laminar diaphragm. The description of the layers of the diaphragm and relevant material issues are listed in Table 6-1.

Figure 6-1. Schematic drawing of the completed piezoelectric diaphragm with view onto the top side of the wafer and a schematic cross section sketch.

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Table 6- 1. Configuration of multilayer structure and materials issues in the fabrication of a materials system for p-MUT diaphragm.

Layer type	Typical composition	Thickness	Purpose of the layer	Fabrication issues
Top electrode	Pt	160 nm	Electrical contact	/
Adhesion layer	Ti	60 nm	Adhesion of Pt to PZT	/
Isolation layer	Polyimide	5 μm	Reduction of parasitic capacitance	Contact holes to bottom electrode
Piezoelectric layer	PZT53/47	2 – 20 pm	Active layer	Crack-free, high densities, patterning, Orientation, patterning
Bottom electrode	Pt	160 nm	Electric contact	Oxidation control: avoids migration through grain of the electrodes
Adhesion layer	Ti	60 nm	Prevents delamination of the electrode and PZT films	/
Membrane material	LTO	250 nm		
	Si ₃ N ₄	500 nm	Mechanical support, diffusion barrier and thermally insulating membrane	Stress control
	SiO ₂	1.8 pm		

The most common sonar transducer shapes are ceramic cylinders, spheres, rectangular bars, bimorphs, and diaphragm. Of these shapes, the diaphragm is most easily adapted to film deposition and silicon micromachining. The diaphragm is roughly comparable in performance to the cylinder when transducers of comparable bandwidth are considered [114]. In this thesis, however, square diaphragm was

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utilized as the active or actuation element, due to the constraints of anisotropic etching of silicon with the diamond structure.

The bottom electrode was patterned to define the elements. Therefore, there is no piezoelectric response for the bond pad or connecting structures. This means that only the diaphragm elements themselves will be sandwiched between two electrodes and will be the only area actuated by an applied voltage.

Three variations of a single device design were fabricated. One major design concern was obtaining a resonant frequency around low end of ultrasonic spectrum. Thus, based on numeral calculation, devices with squared diaphragm of 2 mm × 2 mm, 1.5 mm × 1.5 mm, and 1 mm × 1 mm were fabricated. Moreover, the ratio of active layer thickness to supporting layer thickness is controlled by deep reactive etching (DRIE) of silicon membrane after the deposit of PZT thick film in 3.5 μm and 7 μm thick, respectively.

Since the active part of the device is a thin, multilayer membrane which is supported by a surrounding silicon frame. Thus this diaphragm can be simplified as a peripheral clamped laminate plate. When an external driving electrical field is applied between the top and bottom electrodes of the PZT film, the structure exhibits the controlled movements accordingly. As presented in Figure 6-1, the PZT will expand or shrink in the horizontal direction. The movement of PZT leads to the deflection of the underlying elastic membrane in the vertical direction. As a result, an effective reciprocating driving behavior is realized. For actuators application, the multilayer diaphragm turns input electrical field into bending and stretching of the diaphragm. For sensing application, on the other hand, the multilayer diaphragm turns a input pressure into charge generation. The input pressure is amplified by the ratio

(diameter/thickness)², giving high sensitivity. The output capacitance is also high due to the thin-film dielectric capacitor.

6.2.2 Process development

When developing a processing sequence for fabricating a new device, all aspects of its design and functionality must be taken into account. The mechanical and electrical integrity, and the reproducibility of fabrication of the devices are important.

Devices were fabricated using standard bulk micromachining diaphragm fabrication techniques with some minor modifications necessary for introduction of the PZT thick film. The fabrication flow charts for the diaphragm micromachined ultrasonic transducer are shown in Figure 6-2.

Fabrication starts with double-side polished, 4" diameter by 0.5 mm thick n-type silicon wafers. First, a 1.8 μm silicon dioxide layer was thermally grown on the wafer. Low stress LPCVD Si_3N_4 (500 nm thick) was grown on it, followed by 250 nm of LPCVD low-temperature silicon oxide (LTO). This oxide is typically deposited at a low temperature around $\sim 450^\circ\text{C}$. A standard Ti/Pt bottom electrode layer (60 nm Ti/160 nm Pt) was sputtered on the top of the oxide and patterned by lift-off. The sides of the patterned square bottom electrodes were aligned to be parallel to the $\langle 110 \rangle$ -orientation flat of the wafer.

Patterned opening for membranes were etched through the oxide and nitride on the backside of the wafer, followed by bulk silicon etching in KOH to release the membranes.

After the membrane release, the hybridized sol-gel PZT of composition $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ was deposited upon the wafers (this process has been described in the Chapter 5). The perovskite phase was crystallized by annealing at 700°C and 750°C , respectively. This film was then used for device fabrication, and hereafter is

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referred to as the “device” film. After the PZT deposition and annealing, the PZT layer was wet-etched in diluted HCl: HF solution using a photoresist mask to allow the contact to the bottom electrodes pad.

A 5 μm -thick layer of polyimide was then spun on the wafer, baked, patterned, and cured. Contacts through the polyimide were opened over the diaphragm central sense regions, and the ground plane contact pads. The wafers were then sputter coated with a second Ti-Pt metal layer, which was patterned with a photoresist lift-off process.

Some special process issues related to PZT thick films based micromachined diaphragm are discussed in below.

1. 4” silicon wafer cleaning
2. Dry/wet oxidation of SiO_2 , both side
3. Nitride of Si_3N_4 : LPCVD, both Side
4. LTO coating: LPCVD
5. Bottom electrode coating: Ti, Pt, lift-off, sputtering

Figure 6-2. Schematic design and process flow charts for piezoelectric diaphragm

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6. Backside Si₃N₄ and SiO₂ etching: RIE (CF₄ + O₂)
7. Silicon wet etching: KOH

8. PZT deposition: sol-gel spin coating
9. PZT etching: HCl/H₂O/HF
10. PZT annealing

Figure 6-2 (Continued) Schematic design and process flow charts for piezoelectric diaphragm.

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11. Polyimide coating, patterning and curing

12. Top electrode coating: lift-off, sputtering
13. Backside silicon thinning: DRIE

Figure 6-2 (Continued). Schematic design and process flow charts for piezoelectric diaphragm.

6.2.2.1 Metallization

Choice of the material that forms the bottom electrode layer deserves discussion as it has become an important factor affecting the properties of the PZT layer. Platinum is a widely used electrode material for PZT and similar material systems because it is one of the few noble metals that have low electrical resistance and good stability against oxidation and reaction with the PZT layer during deposition and subsequent high-temperature annealing [138]. However, platinum is known to delaminate if deposited directly on silicon nitride. A solution to this problem is to deposit an intermediate layer to “glue” the platinum electrode layer to the Si_3N_4 layer. Low temperature oxide is known to stick well to Si_3N_4 so that it was deposited on the top of Si_3N_4 . Following the usual practice, titanium was chosen as the adhesion layer between the oxide and platinum because it is known that reaction of oxide layers with platinum will adhere to it under most conditions.

To make microelectronic devices for various applications, it is obviously necessary to pattern the Pt and Ti layers along with the active ferroelectric films. Typically, the Pt on substrate can be patterned by two ways. The first one is to deposit the desired Pt pattern through a shadow mask, which is only applicable for large-sized devices. The second method is to etch off certain parts of Pt using the etching techniques. In some specific cases, such as ferroelectric non-volatile memory, very thin patterns are required due to the tiny size of the device. In these cases, dry etching methods such as ion milling, reactive ion etching (RIE), plasma etching, high density ECR (DECR) plasma etching and inductance coupled plasma (ICP) etching processes have been attempted to etch Pt on Si substrate to make these very small Pt patterns and devices. However, the drawbacks of those dry-etching methods are: (1) relatively low etching rates and long processing time; (2) re-deposition of the sputtered species

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onto the side walls; and (3) big capital investment required for the expensive equipment. In contrast, if the pattern is not so delicate and the size of each pattern is not very tiny, such as in the cases of thin film pyroelectric infrared (IR) detectors and piezoelectric actuators, the wet etching approach can avoid the above mentioned problems related to the dry etching processes. Moreover, the wet etching approach is preferred because it is fully compatible with standard silicon IC processes, and requires low capital investment. However, since platinum is a noble metal, it is difficult to pattern it with common chemicals. Thus Aqua Regia is the chief choice of chemical etchant for Pt [139]. The Pt patterning process was strongly affected by several etching parameters:

- 1) The key challenge is how to choose a proper mask to pattern Pt thin film, since the Aqua Regia is a very strong chemical etchant for most of materials;
- 2) The etching process was very sensitive to the surface cleanness of the Pt film;
- 3) It was also found that the Pt etching rate was strongly influenced by the etching temperature [140].

Accordingly, coating of Pt/Ti layer patterned with lift-off technique is chosen in this thesis. Figure 6-3 shows a well defined Pt/Ti layer on LTO/Si₃O₄ by the lift-off technique.

An important experimental result was that Ti/Pt metal layers electron-gun evaporated at room temperature tend to have higher tensile stresses than layers sputtered at 300 ~ 400 °C. As a result, the electrode/PZT film stack cracked and peeled off when deposited on the evaporated metal layer. Therefore, sputtered Ti/Pt layers were utilized here.

After the deposition of PZT films, the substrates must be treated at high temperature in order to achieve adequate sintering of PZT particles in the composite

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films. This high-temperature process results in a reaction between the PZT and substrate. This reaction occurs irrespective of any passivation layers or electrodes present, and results in sites consisting of a small pore at the centre of a radial pattern of material. These reaction sites are scattered around PZT and to the naked eye appear like a speckling effect on the surface of the substrate. This reaction also clearly occurs under the bottom electrode and results in bubbles, as shown Figure 6-4. These bubbles are clearly undesirable since they undermine the adhesion of the Pt/Ti electrode. Accordingly, annealing PZT films at 750°C for 1 hour is the uppermost acceptable processing temperature.

Figure 6-3. Patterned Pt/Ti bottom electrode layers on LTO by lift-off process.

Figure 6-4. Blisters in the Pt/Ti layers after high temperature annealing.

6.2.2.2 Backside etching

The membrane was obtained by silicon bulk micromachining in hot KOH. A stress compensated bilayer of thermal oxide (SiO_2) and LPCVD nitride (Si_3N_4) was applied as the mask layer. The first lithographic step consisted of opening this mask layer by dry etching (CF_4) for the definition of the membranes. The alignment between the masking layer and pre-patterned Pt/Ti bottom electrodes was carried out on a Karl Suss MA6 double side aligner, as shown in Figure 6-5. Well defined photoresist before etching is given in Figure 6-6.

The KOH solution was mixed to a ratio of 44 g potassium hydroxide crystals to 100 ml de-ionized water and heated to 80°C . The samples were given a 30 seconds dip etch in 7: 1 buffered HF (BHF) to remove any native oxide prior to etching. This dip was short enough to avoid the effects of the BHF. The Si etch rate is normal for the bulk of the substrate at approximately $0.86\ \mu\text{m}/\text{min}$. The thickness of the left Si was checked every 1 hour using a surface profilometer.

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For the use of membrane, a uniform smoothness of silicon throughout the element size is necessary. The application of chemical etching to micromachining requires a revelation of surface of mirror like quality. If a mask pattern is properly aligned, minimal underetching is achieved, which is of special importance for deep etching. The etchants used for micromechanic structures must yield a smooth surface and satisfying anisotropy, i.e., large value of $V_{100}:V_{111}$ ratio, where V_{hkl} is etching rate of (hkl) plane. Therefore, to achieve good surface (100) smoothness, a solution with high anisotropy must be used, i.e., it must have an etching rate (100) plane which is different as compared with other planes. This requirement is fulfilled by high concentrated hydroxides alone, where the etching rate of (100) plane is lower than other high-indexed ones [141-145]. In summary, the higher etching anisotropy, the lower under etching to the mask, then the smoother the silicon cavity bottom surface.

Anisotropic properties of silicon, as shown in Figure 6-7, are the cause of various shapes of structures obtained under etching, depending on the solution composition, since etching rates of individual planes (hkl) and their ratios $V_{h1k1l1}:V_{h2k2l2}$ are closely related to the solution used. During anisotropic etching in each crystallographic zone, planes with minimal etching rate are developed. The holes or islands are limited by planes with minimal etching rate in proper crystallographic zone. As a result of holes etching, planes of relative high etching rate, belonging to specifies crystallographic zones disappear. Thus holes are limited with planes of low etching rates.

The KOH etchant is attacking the silicon at the electrode/substrate interface and hence undermining the adhesion of the electrode. This may also cause cracks in the Pt/Ti film where the etchant can attack the silicon [146].

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After the silicon etching, the membranes were examined in both scanning electron and optical microscopes. SEM images in Figure 6-8 and Figure 6-9 give the cross-section and top-view of resultant silicon membrane. The silicon left was controlled to be about 10–20 μm thick. It is clearly shown that both the side (111) plane and bottom (100) plane are mirror-like, which means that a perfect anisotropic etching has been achieved along the crystallographic direction.

Because the etching rate of $\langle 100 \rangle$ direction is 400 times faster than that of $\langle 111 \rangle$ direction, an undercut of 1–2 μm was observed in Figure 6-10. In respect of a diaphragm with width dimension in hundred microns, the influence of undercut could be neglected.

Therefore, the good quality, crack-free membrane is mechanically strong enough to support the micromachined piezoelectric diaphragm (p-MUT), which may have each element size in the range of 0.25 mm $\times$ 0.25 mm to 2 mm $\times$ 2 mm.

All the devices fabricated used a square membrane as the sensing element, due to the limitation of anisotropic etching in diamond-cubic silicon. New fabrication techniques (such as through-wafer plasma etching) allow the fabrication of circular devices, whose greater symmetry should improve performance and enhance the strength.

Figure 6-5. Double side alignment from back side - Karl Suss MA6.

Figure 6-6. Patterned alignment mark on the backside of the wafer, with photoresist on it.

Figure 6-7, Anisotropic wet etching of (100) silicon: the slowest etch rate in the $\langle 111 \rangle$ direction and the fastest in the $\langle 100 \rangle$ and $\langle 110 \rangle$ directions.

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Figure 6-8. Cross-section of a 20 μm thick wet-etched silicon membrane structure.

Figure 6-9. Top view a silicon cavity array.

Figure 6-10. Microscope image of the undercut of masks layer during silicon anisotropic wet etching.

6.2.2.3 PZT coating and patterning

In recent years, PZT thick film has been of great interest for its potential applications in MEMS. Deposition PZT thick films on a platinum coated silicon wafer and patterning it into designed dimension constitute the two most significant challenges during its integration with micromachining technologies for MEMS fabrication. It is also one of the major research objectives of this thesis.

As reviewed in Chapter 2, there has recently been a great deal of research in ferroelectric thin films on silicon for use in ferroelectric random access memories (FRAMs) and dynamic random access memories (DRAMs) [114]. Many techniques are used to deposit these films, including sol-gel, RF sputtering, laser ablation, and chemical vapor deposition (CVD). For memories, a large capacitance in a small area (for DRAMs) and low coercive voltage (for FRAMs) is desired. Hence, films less

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then 300 nm thick are typically used. On the contrary, for piezoelectric actuator application, thicker films are desirable to maximize the sensitivity of displacement/voltage.

In this thesis research, large area pinhole-free films of lead zirconate titanate (PZT) up to 20 μm in thickness have been fabricated on 4-in silicon wafers by the hybridized sol-gel process. Details of the deposition process have been presented in Chapter 5. The mole ratio of Zr to Ti is maintained at 53: 47, the morphotropic phase boundary composition (MPB). The precursor solution is 40 wt% PZT xerogel in MOE. PZT powder was sintered for crystallization and ball milled before dispersed into the sol-gel solution with vehicle. Films were fabricated on 4-in silicon wafers with platinum-base electrodes by the spin-coating process. The spin rate was 100 rpm for 5s whereafter 2000 rpm for 30s. The films were dried at 250°C to evaporate the solvent, and then rapidly heated to 500°C to remove the residual organics. This procedure was continued until films of the desired thickness were obtained. The films were finally annealed at 700°C and 750°C for 1 hour, respectively. Film thickness was measured with a Dektak profilometer after patterning the films.

After the Ti/Pt top electrode was sputtered, dielectric, ferroelectric, and piezoelectric properties were measured. There were no electrical shorts in any of these test structures. Figure 6-11 shows the X-ray diffraction result of a device PZT film after the device fabrication. Pure perovskite phase is observed which means that the succeeding fabrication process after PZT films deposition had negligible effect on the PZT layer. The weak field dielectric constant of the film at 1 kHz is about 650, with low dissipation losses of 2%, as indicated in Figure 6-12. The hysteresis loops for the 3.5 μm and 7.0 μm thick films are shown in Figure 6-13.

Figure 6-11. X-ray diffraction spectrum of a device PZT films in 3.5 μm thick annealed at 700°C for 1 hour.

Figure 6-12. Low field dielectric properties of PZT thick films.

Figure 6-13: Polarization-electric field hysteresis loops of PZT thick films.

After the PZT thick film has been successfully deposited, it has to be patterned into required shape with designed dimension to act as an active layer in microelectromechanical systems. Lithography and etching are the key steps to define the film's geometry and to manufacture MEMS diaphragm.

The standard lithographic process was adopted to pattern the photoresist, which was used as etching masks. Photoresist was spin-coated onto the PZT film at 4000 rpm for 30 seconds. After coating the first layer, the wafer was baked at 90°C for 2 minutes, and then a second layer of photoresist was coated. The final thickness of the photoresist was about 1.8 μm. After the photoresist had been soft-baked at 90°C for 10 minutes, a double side Karl-Suss MA06 mask aligner was used to pattern the photoresist with the mask. The patterned photoresist was then hard-baked at 110°C in oven for 30 minutes.

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One important requirement for the lithography step used here is good adhesion between the PZT film and photoresist, since long etching time in HF-based solution is used for patterning thick PZT films after photolithography step. The type of photoresist used as the mask could also affect the PZT etching process. From the results of W. G. Liu et al. [140], diluted 10: 1 HF solution was more reactive with photoresist AZ1518 than photoresist AZ5214E. In order to obtain a longer processing time before the etching mask is delaminated from under PZT films, photoresist AZ5214E was employed. Moreover, hexamethyldisilazane (HMDS) was used to promote adhesion between photoresist and underlayer during lithography. HMDS is one of the most commonly used adhesion promoters for silicon oxide and photoresist in MOS processing. It was spin-coated on the PZT film before spinning photoresist.

There are two approaches to pattern the PZT film: dry etching and wet etching. For the first one, reactive ion etching (RIE) using capacitive [147], inductive [148], or electron cyclotron resonance (ECR) plasma [146, 149] has been utilized to pattern PZT films. These studies were driven primarily by ferroelectric memory applications. The film thickness in these applications generally does not exceed 250 nm. It has been reported that it is difficult to form volatile species from PZT with etching gases at room temperature; hence, heating the substrate or increasing the ion bombardment energy is generally required for dry-etch patterning. As a result, the etch rate and selectivity with respect to photoresist developed in the above methods are not suitable to etch PZT films for MEMS applications which require 2 to 20 μm thick PZT films.

With regard to wet etching the chemical etchants used for the PZT thick films need to be compatible with photolithography processes. PZT ceramics can be etched by HCl, HF, H_3PO_4 , HNO_3 , H_2SO_4 , NaOH, and KOH. However, neither H_2SO_4 nor the basic solutions (NaOH, KOH) are suitable here, since photoresist is quickly

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stripped off in these solutions. In addition, the etch rate for H_3PO_4 and HNO_3 is slow. Therefore, three wet etching recipes, 0.34%HF: 5%HCl: 94.66% H_2O at room temperature, HF at room temperature and HCl at 45 °C, were adopted and compared by L. P. Wang et al. [150].

However, there were some problems with each etchant. For the first recipe, residue on the etch area could not be removed even for a long etching time (30 minutes); consequently, the photoresist was delaminated from the PZT films. A whitish residue was clearly observed after drying the sample. Adjusting the ratio of HF and HCl did not lead to markedly different results. With HF alone at room temperature, residue formation was still a problem. Furthermore, the photoresist was delaminated from the PZT films after only 10 minutes of etching. With HCl at 45 °C, residue was not a problem. However, patterns with feature sizes smaller than 50 μm could not be patterned, since HCl quickly etched the PZT films by dissolving material along the grain boundaries. This also resulted in severe undercutting, and overall this etching process was difficult to control. Since the wet etching process is isotropic, lateral etching cannot be avoided. One way to describe the degree of undercutting is the ratio of lateral to thickness etching. Table 6-2 summarizes the results of the above etching recipes.

An additional problem related to the Ti/Pt electrode layer during PZT etching is that Ti is known to diffuse along the grain boundaries to the surface of the Pt film. At the surface, the Ti is free to react with available species, contaminating the surface of the Pt film. Problems do arise during the etching of the PZT films in HF. Ti and Titanium oxides are etched by HF and the diffusion pathways along the grain boundaries permit the HF to reach the underlying titanium, titanium dioxide, and silicon dioxide layers. If HF reaches these layers it will attack them and undercut the

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Pt electrode layer. It is by such a way that the delamination spirals are thought to form. This typically requires prolonged exposure to HF (>10 minutes).

From the above comparisons, it is apparent that residue formation resulted from the use of HF-based solutions. X-ray diffraction indicates that they primarily consist of the metal fluorides, $\text{Pb}_{0.85}\text{Zr}_{0.15}\text{F}_{2.3}$ and $\text{Pb}_5\text{ZrF}_{14}$, which have a very low solubility in the etching solution. It was found that these residues can be quickly removed by HCl in a short time (–30 seconds).

From the above results, no single etching step was found that can provide a residue-free surface, good selectivity, and limited undercutting for thick film PZT patterning. Consequently, a two-step etching process has been successfully developed by L. P. Wang et al. [150] as in Table 6-3. In the first step, 10:1 buffered HF was used to remove the majority of the film at room temperature. Then a solution of 2HCl:H₂O at 45 °C is used to remove metal-fluoride residues remaining from the first step. This enabled successful patterning of PZT films up to 8 microns thick. A high etch rate (0.13 $\mu\text{m}/\text{min}$), high selectivity with respect to photoresist, and limited undercutting (2:1 lateral: thickness) were obtained.

However, their two-step etching process still has a severe undercut (2:1) since the second step of dipping in HCl quickly attacked the PZT films from the sidewalls even if a short etching time. For most MEMS devices, although, such an undercut is acceptable since the feature size in MEMS is relatively larger than in microelectronics. The diffusion of etchant into PZT films, on the other hand, might affect the electrical properties of the piezoelectric active layer. In the thesis, the definition of PZT films was partially avoided by defining the diaphragm elements with bottom electrode patterning. Etching of PZT films is only necessary to be processed for opening a window in it for bottom electrode bonding pad contact.

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With regard to etchant recipe optimization, we might conclude from the above results that the HF concentration should be low to prevent delamination of photoresist from PZT films and to reduce the whitish residue. Higher HCl concentration is desired to obtain a higher etching rate. Due to the difficulty in controlling the procedure, it should not be too high either. Therefore, we chose the 50:50:0.1 HCl: H₂O: HF chemical solution as the etchant recipe. The etching rate at room temperature was about 0.8 μm/min. The formation of whitish residue during PZT film etching was depressed by rinsing and nitrogen drying the wafer after every two minute etching.

Table 6-2. Comparison of different etching recipes for PZT thick films [150].

Etching recipe	Etch Rate	Resist	Undercut (lateral to thickness)	Residue
0.34%HF, 5%HCl, 94.66%H ₂ O at 25°C	~ 0.2 μm/min	Delaminated after ~ 30 minutes	3:1	Whitish residue
HF at 25°C	~0.15 μm/min	Delaminated after ~ 10 minutes	2:1	Whitish residue
HCl at 45°C	~1 μm/min	Does not provide good protection	10:1	Clean surface

Table 6-3. Two-step etching process for thick PZT film patterning [150].

Step	Process	Remark
1	BOE (10:1) etching at room temperature	Rate: 0.13 μm/min
	DI water rinsing and nitrogen gun drying	Whitish residues on the etched area
2	2HCl:H ₂ O at 45°C	Time: 30 seconds
	DI water rinsing and nitrogen gun drying	Clean surface

6.2.3 Characteristics of diaphragm oscillator p-MUT

In this section, deflection characteristics, as well as the results of frequency response of the various fabricated diaphragm transducers are presented.

The basic transduction characteristics of the devices were analyzed using a Polytec vibrometer working with a laser interferometer. The experimental configuration is shown in Figure 6-14. In this measurement system, a homodyne interferometry which makes use of two light beams of identical frequency (wavelength) is utilized. Since displacement in samples produces the change of interference fringes, the displacement information is encoded in the amplitude of the photocurrent corresponding to the interference fringe through a photodetector. There are two main optical schemes for homodyne interferometers: the single-beam Michelson and the double-beam Mach-Zender systems. The former system measures the displacement of only one surface and the latter characterizes two surfaces of the samples. In this experiment, one split laser beam is focused onto the front surface of the operating device by reflection, whereas the other split of the laser beam for referring is reflected by an attached mirror.

A programmable HP3245A universal source is used for voltage application to drive the diaphragm transducer and an ultrasonic deflection is generated. With the displacement decoder and velocity decoder, such a deflection detected by laser beam is transformed into voltage signal. If a voltage drives the piezoelectric at a frequency f , the piezoelectric motion will also be of frequency f , since piezoelectric constant represents the linear relation between the strain and applied field. Whereafter the output signal was filtered using a low-noise preamplifier to eliminate signals at

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different frequency. The output spatial waveforms of the deflection were recorded by a digital oscilloscope and HP dynamic signal analyzer.

For the piezoelectric measurements described here, a DC bias of 30 V was employed, and the peak-to-peak potential was varied between 0 and 50 V. The fi-equency spectrum was measured by scanning through the frequencies between 100 Hz and 300 kHz.

Although these measurements cannot be used to calculate the piezoelectric coefficients of the film, they can be used to obtain a non-destructive measurement of the deflection of the diaphragm induced by the piezoelectric response of PZT film.

Figure 6-14. Configuration of testing system fi-om diaphragm deflection using single beam laser beam.

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6.2.3.1 Deflection of P-MUT diaphragm

Deflection of the diaphragm is an important feature for the microphone and microspeaker diaphragm structure.

When an external driving electrical field is applied between the top and bottom electrodes of the PZT film, the PZT will expand or shrink in the horizontal direction, as presented in Figure 6-1. The movement of PZT leads to the deflection of the underlying elastic membrane in the vertical direction. The response of the central point of a square 1.5 mm x 1.5 mm p-MUT diaphragm driven by 3.5 μ m-thick PZT film with unipolar sine wave electric field is shown in Figure 6-15. The peak-to-peak driving voltage is 10 V (all of the driving voltage here is referring to p-p value) at a frequency of 500 Hz. A DC bias voltage of 30 V was superimposed at the same time. The amplitude of diaphragm deflection is 13 nm and it is constant in the frequency range up to 40 kHz. There is no phase shift between the excitation signal and the diaphragm response. Because the diaphragm deflected downwards whereas the z axis is defined as upwards, the wave form of the diaphragm response is exactly in inverse to that of the excitation signal.

Figure 6-16 shows the dependence of deflection response on the driving voltage of a square 1.5 mm x 1.5 mm diaphragm under 50 V sine wave exciting signal and 30 V DC bias. The amplitude of the deflection is proportional to the applied voltage for the unipolar drive and is about 50 nm when applying 50 V driving voltage at a non-resonant frequency of 500 Hz.

The deflection amplitude of the square 1.5 mm x 1.5 mm diaphragm versus driving voltage is shown in Figure 6-17. It was found that the amplitude was increased linearly with the applying voltage in the range of applied voltage. The dot line is a linear fitting result. The slope of it is 1.05, with a reliable factor of 0.997. However,

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with driving voltage further increased, the curve should deviate from the linear relationship and the slope of the curve was gradually decreased. Finally, the curve showed a saturation tendency [151, 152].

The relationship between the deflection amplitude and the element width of the square p-MUT diaphragm is presented in Figure 6-18. The deflection amplitude was approximately linearly increased with the element area of the PZT based p-MUT diaphragm transducers. The dash line of linear fitting result with a slope of 9.69 indicates that square diaphragm could be designed to achieve a certain center point deflection required through adjusting the element width size.

Figure 6-15. Sine wave Dynamic response of 1.5 mm x 1.5 mm square p-MUT diaphragm driven by 3.5 μm thick PZT film with a 30 V DC bias.

Figure 6-16. Displacement response of a 1.5 mm x 1.5 mm square diaphragm, with 30 V DC bias superimposed.

Figure 6-17. Voltage dependence of the deflection amplitude of the p-MUT diaphragm with 1.5x1.5 element size.

Figure 6-18. Deflection of the diaphragm vs. the dimension size of square element.

6.2.3.2 Frequency responses

To evaluate the dynamic response in a wide frequency range, measurements were carried out using a sine-wave signal. The results of this measurement for square diaphragm with $2\text{ mm} \times 2\text{ mm}$, $1.5\text{ mm} \times 1.5\text{ mm}$, and $1\text{ mm} \times 1\text{ mm}$ elements size driven by a $3.5\text{ }\mu\text{m}$ thick PZT film are presented in Figure 6-19, Figure 6-20, and Figure 6-21, respectively. These devices were operated under 30 V DC bias and 30 V p-p driving voltage. As indicated in the figures, the first resonant frequencies for these cases are 31.6 kHz , 57.75 kHz and 124.5 kHz , respectively.

The frequency dependence of the deflection and phase shift for a $2\text{ mm} \times 2\text{ mm}$ size square diaphragm is presented in Figure 6-22. The phase shift between the excitation signal and the deflection was not observed up to 40 kHz .

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It is found that the resonant frequency values decrease rapidly with the increase of the width, especially in the small width range. For the PZT films with thickness of 3.5 μm , the resonance frequencies of the diaphragm with width of 2 mm to 1 mm are at the range of 40 to 150 kHz. This frequency range is particularly suitable for the ultrasonic audio beam application. Figure 6-23 shows the relationship between the width of square laminar diaphragm and their first resonant frequency. A simple and linear relation on resonant frequencies could be obtained as we change x-coordinate into the reciprocal of area of diaphragm, $1/a^2$, shown in Figure 6-23 (b).

As shown in Figure 6-1, the cross section of the structure of an element of the diaphragm ultrasonic transducer can be simplified as a laminated structure. The first resonant frequency depends on the thickness t and the size a of the diaphragm. Simple analytical formulas are available for the resonant frequency. For a diaphragm which is fixed on all edge sides on relative thin membrane, the first resonant frequency of such a square diaphragm could be calculated as follows [153-155]

$$f_r = \frac{35.99}{2\pi \cdot a^2} \sqrt{\frac{Y}{(1-\nu^2)\rho \cdot t}} \quad (6-3)$$

where Y is elastic modulus, ν is Poisson's ratio, ρ is density, a and t are edge length and thickness of the diaphragm, respectively. Using the material constant and dimensions of the diaphragm, the resonant frequency of the diaphragm could be derived. It indicates that the first resonant frequency is inversely proportional to the square of element size, a^2 , and to the square root of the diaphragm thickness (t)^{-1/2}.

As for a disk diaphragm with certain thickness, the first resonant frequency could be expressed as [156]:

$$f = 1.654 \cdot \frac{t}{a^2} \cdot \sqrt{\frac{Y}{\rho(1-\nu^2)}} \quad (6-4)$$

Then for this case the first resonant frequency is proportional to $\frac{t}{a^2}$.

As was mentioned above, these devices were characterized with a DC bias applied between the top and bottom electrodes in order to pole PZT, and keep it poled, as the device was operated. To determine the effect of bias on the first resonant frequency, a very narrow frequency sweep was performed as the bias voltage was varied. One of the results is given in Figure 6-24. When a DC bias voltage is added to the driven signal, the resonant frequency is shifted to higher frequencies. It could be due to piezoelectric stiffening of the PZT layer resulting from the applied bias. In other words, the applied bias indeed increases tensile stress that may translate into forces that stretch the membrane, and thus increase the frequency.

The above formulas derived for resonant frequencies calculation, therefore, should also be modified with considering the stresses.

for diaphragm on membrane with smaller thickness:

$$f_r = \frac{35.99}{2\pi \cdot a^2} \sqrt{\frac{Y+T}{(1-\nu^2)\rho \cdot t}}; \quad (6-5)$$

for diaphragm on disk with larger thickness:

$$f = 1.654 \cdot \frac{t}{a^2} \cdot \sqrt{\frac{Y+T}{\rho(1-\nu^2)}} \quad (6-6)$$

where the stress T is added to the elastic modulus Y.

On the other hand, very high compressive or tensile stresses can appear within the layers because of the different thermal expansion coefficients (for high temperature growth processes) or because of the intrinsic mismatch between two materials (related to crystallographic mismatch or to growing conditions of the films). All of them could heavily affect the resonant frequencies; and the stresses in the systems should be reduced to a low acceptable level.

It can also be seen from Figure 6-24 that the diaphragm decreased from larger bias voltage has a higher resonant frequency than that increased from smaller bias voltage. It could be ascribed to that the PZT film in diaphragm is more effectively poled under the higher bias than that under the lower bias.

According to the equation (6-5) and equation (6-6), for not too small thickness, the membranes are in principle well approximated by the model for thin clamped square-shaped disk, for which exact values of the resonance frequencies are available [156]. In the limit of zero thickness, pure membrane behavior should be observed.

If the spectrum of the same membrane was measured for different silicon thickness, a crossover from membrane to disk behavior could indeed be observed: the $h^{-1/2}$ slope for small silicon thickness (h) changes to a slope proportional to h for greater thickness, as expressed in the above equations. The diaphragm is obviously under a small tension, leading to the frequency increase at small thickness.

After the backside silicon has been thinned down by DRIE technique, as shown in Figure 6-25, the resonant frequency of a 2 mm × 2 mm diaphragm increases from 31.6 kHz to 42.1 kHz, and the static deflection amplitude decrease at the same time, it is consistent with the calculated results of P. Muralt [157] for a membrane structure (Figure 6-26 and Figure 6-27).

As a result, after the device fabrication finished, i.e., the thickness of the PZT film should be set at the manufacturable maximum and then the thickness of the silicon layer could be adjusted by DRIE to achieve the desired resonant frequency.

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Figure 6-19. Frequency response of deflection of square 2 mm x 2 mm diaphragm driven by 3.5 μm thick PZT film, under 30 V driving voltage with 30 V DC bias.

Figure 6-20. Frequency response of deflection of square 1.5 mm x 1.5 mm diaphragm driven by 3.5 μm thick PZT film, under 30 V driving voltage with 30 V DC bias.

Figure 6-21. Frequency response of deflection of square 1 mm × 1 mm diaphragm driven by 3.5 μm thick PZT film, under 30 V driving voltage with 30 V DC bias.

Figure 6-22. Electric-field-induced deflection responses vs. frequency.

Figure 6-23 Change of the first resoant frequency of structure via the variation of dimension of squared diaphragm, (a) width a and (b) inverse of square of width, $1/a^2$.

Figure 6-24. Resonant frequency vs. DC bias. (for 1.5 mm × 1.5 mm element size).

Figure 6-25. Frequency response of deflection of square 2 mm × 2mm diaphragm driven by 3.5 μm thick PZT film, under 30 V driving voltage with 30 V DC bias. DRIE process was applied to reduce the silicon membrane thickness.

Figure 6-26. Calculated amplitude of the static deflection for the case of the response of an unpoled film at zero d.c. bias and 5 mV a.c. electric excitation at 1 kHz. The experimental points have been obtained by a series of etching steps on the same device [157].

Figure 6-27. Resonance frequencies as a function of the silicon thickness of 2 mm diameter diaphragms with sputtered PZT films [157].

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6.2.3.3 Transmitter characterization

Acoustics is a domain of predilection for piezoelectric materials due to several reasons [158]:

- The linearity of the piezoelectric response in both direct and converse effects allows a simple electronic circuit for driving or reading the transducers;
- The high density of elastic energy that can be handled in a small volume of material is of primary interest for applications requiring a large acoustic power using a limited space;
- The high speed of sound in most of the piezoelectric materials offers the possibility of having a fast response and a wide operating bandwidth;
- Piezoelectricity allows generating and sensing vibrations on a large dynamic range and a wide frequency band.

To measure acoustic frequency response of the diaphragm ultrasonic transducers when used as transmitters, the fabricated devices were driven by 10 V AC voltage under 30 V DC bias application. A standard microphone was set at a point 10 mm from the front surface of devices. The driving voltage here is referring to p-p value.

Figure 6-28 and Figure 6-29 show the frequency dependence of output sound pressure of a single diaphragm with dimension size of 1.5 mm × 1.5 mm and 2 mm × 2 mm, respectively. According to frequency spectrum, the acoustic resonant frequencies were observed as 57.6 kHz and 31.5 kHz. Both of them are consistent with the results from deflection measurement of 57.75 kHz and 31.6 kHz.

The output sound pressure of a transmitter can be evaluated by sound pressure level (SPL), which can be expressed by

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$$SPL = 20 \log \left(\frac{P_{rms}}{P_{ref}} \right). \tag{6-7}$$

Reference sound pressure (P_{ref}) is 20×10^{-6} Pa.

The SPL of a single $1.5 \text{ mm} \times 1.5 \text{ mm}$ size diaphragm transmitter is shown in Figure 6-30, as a function of the driving voltage. As the driving voltage increases, the SPL also increases. Such a diaphragm has SPL of more than 100 dB throughout the driving voltage range. The static pressure capability is adequate for many acoustic applications, where a SPL of at least 50 dB is needed.

Figure 6-28. Frequency dependence of sound pressure of a single diaphragm with size of $1.5 \text{ mm} \times 1.5 \text{ mm}$.

Figure 6-29. Frequency dependence of sound pressure of a single diaphragm with size of 2 mm × 2 mm.

Figure 6-30. Output sound pressure level (SPL) vs. driving voltage.

6.3 Design and fabrication of MEMS piezoelectric ultrasonic transducer array

The major type of transducer utilized in an ultrasonic speaker is the simple piezoelectric transducer normally used for buzzers. For an application that composes of multielements, actuation has generally been accomplished placing bulk discrete ceramic transducer elements. Examples of such structure are ultrasonic and surface acoustic wave transducers and arrays, unimorph and bimorph actuators, inkjet printer heads and active damping systems. However, common problems in the implementation of such a device are the cost and complexity of assembly, the method of interconnection of the incorporation of external circuits, and limited opportunities for batch fabrication. Therefore, forming transducers arrays in silicon, that some of the electronics could be fabricated integrally with transducers, have been developed and studied in this thesis.

In very recent years, micromachined ultrasonic transducers (MUT) have been investigated for phased arrays in high frequency acoustic imaging to overcome resolution and frequency limits of reticulated bulk PZT transducers used today. The basic element consists of a micromachined membrane that is driven by either piezoelectric actuation (p-MUT) [114, 159] or capacitive [160]. Array sensors/actuators for underwater are widely used for various applications such as fish finder and human body diagnosis; and even its image is available for medical examination of an unborn child and heart.

However, ultrasonic microsensor and actuator array for in-air use have little been investigated. Ultrasound is significantly absorbed in air contrary to underwater environment. The absorption is in proportion to square of frequency, and propagation distance is less than a few meters in the frequency range order of hundreds of KHz

[161]. Therefore, design and fabrication of a phased array of ultrasonic transducers for in-air used is a challenging area that is worth to explore.

In this section, a 2-D ring phased array using micromachined ultrasonic transducer diaphragm working at low frequency was designed and fabricated. The array is designed for sharp directivity considering wavelength of ultrasonic in air and the chip size for micromachining application.

6.3.1 Design and photomask layout of micromachined ultrasonic transducers phased array for in-air use of loudspeaker

It is known that the ultrasound wavelength determines directivity pattern of actuator/sensor array when the elements are arranged regularly at equal spacing [153]. Sharpness of the directivity is almost in proportion to the ratio of the size of array to the wavelength [162], and large spacing between adjacent elements makes large side lobes when the wavelength is fixed [163]. Furthermore, a ring array is slightly more efficient than a matrix array in the terms of directivity to the same number of elements [164]. The directivity of any arrangement of array can be obtained by Eq. (6-9):

$$F(\theta, \phi) = \frac{1}{N} \sum_{i=1}^N |f_i(\theta, \phi)| \quad (6-9)$$

where

$$f_i(\theta, \phi) = \frac{1}{a^2} F_0 \cos \theta \int_{y_i-a/2}^{y_i+a/2} \int_{x_i-a/2}^{x_i+a/2} e^{(jk\rho \sin \theta \cos(\theta-\phi))} dx dy \quad (6-10)$$

$$\phi = \tan^{-1} \left(\frac{y}{x} \right), \rho = \sqrt{x^2 + y^2} \quad (6-11)$$

N is the number of elements, (x_i, y_i) is the center position of i -th elements, and k and F_0 are wave number and intensity of ultrasound, respectively.

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Therefore, the basic design parameters for a transducer array include working frequency (f), number of elements (N), interelement spacing (d) and element size of width (a).

As discussed above, the working frequency of an ultrasonic transducer array for use of in-air loudspeaker, low frequency ranging from 20 kHz ~200 kHz is required. To obtain a sharp directivity, a larger N is preferred [165]. Moreover, with multiple elements the beam profile (focus, beam width and direction) of an array can be controlled electronically. The larger the number of the elements in the array is, the more variable beam profile and the fewer devices needed to be moved. Array with different elements were designed in thesis with varying the number of element ring. To eliminate unwanted side lobes in the beam pattern, the interelement spacing (d) was chosen as $\lambda/2$. Since the speed of sound in air is 346 m/s, d was designed to 2.2 mm with regarding to a working frequency of 70 ~80 kHz. It is evident that the larger the array elements are, the higher the induced pressure is. It's thus desirable to make the element size (a) as wide as possible without sacrificing the other transducer performances, particularly for inspecting large members that demand large pressure. On the other hand, it has been found that the influence of element width is small if the width is less than half the wavelength [165]. Thus, the element size, a , was chosen as 0.5 mm with the chosen interelement spacing.

The photo mask designed consists of 5 layers are given in appendix A. Five types of array arrangement was placed on the mask: one ring array consisting of 7 elements, two ring array consisting of 19 elements, three ring array consisting of 37 elements, four ring array consisting of 61 elements, and three ring array without the inner ring array consisting of 30 elements. The element composing arrays is square

with $0.5\text{ mm} \times 0.5\text{ mm}$ piezoelectric diaphragm, and the spacing between them is 2.2 mm. One of the arrays with 3 rings of element designed is shown in Figure 6-31.

As described in previous section in this chapter, the diaphragm element was defined by bottom electrode patterning. The electrical connections are all brought to the edge of the array, thus they can be wire bonded to a conventional flat-pack. A polyimide interlayer dielectric was used to reduce the parasitic capacitance which would be caused by the long interconnect lines pass under PZT alone.

Figure 6-31. Phased ultrasonic array consisting of 3 rings of element for use of in-air loudspeaker use.

6.3.2 Optical observation

Micromachined, kHz-range two-dimensional transducer phased array for miniaturized, in-air use beam loudspeaker have been developed using ferroelectric thick films and silicon bulk-micromachining technologies. Figure 6-32 shows an optical photo of the final devices, details of some examples of the arrays are given in Figure 6-33.

After the devices fabrication, the membranes were examined in both scanning electron and optical microscopes. On the front side of the sample, no discontinuity of any type was observed in the entire area of the membrane. The PZT/Pt/Ti/LTO/Si₃N₄/SiO₂/Si multilayer, as shown in Figure 6-34, appears untouched by etchants; and films adhesion remained good. Also no buckling or bulging of the membranes could be seen. The lack of deformation of the membrane structure indicates that the stress in the PZT film was under control and negligible during the device fabrication.

This micro-machined ultrasonic transducer array can be used as the ultrasonic phase array, audio beam emitter and receiver, acoustical sensing and detection in various applications.

Figure 6-32. Ultrasonic array on 4-in silicon wafer.

Figure 6-33. Example of a 4-ring (left) and 2-ring (right) ultrasonic array.

Figure 6-34. Multilayer structure of the final device.

6.4 Summary and conclusions

This chapter has presented a new combination of micromachining and thick PZT film to form miniaturized transducers for ultrasonic application. Composite sol-gel PZT thick films were deposited on Pt/Ti/LTO/Si₃N₄/SiO₂/Si substrates. Square diaphragms ranging from 0.5 mm to 2 mm were fabricated. Phased transducer arrays with 2 to 5 rings have fabricated. Deflection amplitude, frequency response, and acoustic transmitting properties were investigated.

CHAPTER 7 CONCLUSION AND RECOMMENDATIONS

7.1 Conclusion

This thesis has aimed at developing, characterizing and evaluating ferroelectric/piezoelectric PZT thick films for MEMS type device applications that could be integrated with silicon micromachining. The basic requirement for such applications is that the ferroelectric/piezoelectric PZT films should have crack-free, dense and uniform microstructure; tens of microns in thickness to produce required displacement or driving force; typical and acceptable ferroelectric and piezoelectric properties with reasonable high dielectric constant.

The thesis accomplished the following: 1) developed a novel hybrid processing technology by combining fine-sized PZT powder and sol-gel process; 2) evaluated the low temperature processing characteristic of this novel hybrid sol-gel composite technique and its application to screen-printed thick films and bulk ceramics; 3) deposited crack-free, dense and uniform PZT composite thick films on platinum coated silicon substrate; 4) optimized the novel hybrid sol-gel composite technique in terms of microstructure, dielectric and ferroelectric properties of the coated PZT thick films; 5) studied the integration of PZT composite thick films and silicon micromachining techniques, explored the potential applications of the derived films as ultrasonic transducer in MEMS type devices.

7.1.1 Hybrid sol-gel composite technique

A novel hybrid technique based on nano-sized powders and homogenous matrix of sol-gel precursor composite has been developed. The key of this novel hybrid processing technology is the combination of the nano-sized particles and sol-gel precursor. Nano-sized particles could be produced from commercially available PZT powder using the high-energy ball milling technique. Xerogel, the sol-gel precursor, could be decomposed and crystallized at low temperature ranging from 300 to 500°C. According to the XRD results of heat treated xerogel, perovskite-dominant structure remained in the resultant materials. Pyrochlore intermediate phase was not observed, indicating that a direct amorphous to perovskite phase transformation has been proposed. With this novel processing approach, high density of green bodies can be achieved; agglomeration between particles can be eliminated; low crystallization temperature can be realized; and sintering temperature to get fully dense materials can be remarkable reduced.

7.1.2 Low temperature processed screen-printed thick films and bulk ceramics

Dense materials both in films and bulk ceramics, therefore, can be readily obtained at low processing temperature using this novel hybrid sol-gel composite technique. Screen-printed PZT thick films on Au/Al₂O₃ and bulk ceramics, with sub-micron grains, can be produced with the sintering temperature decreased from 1100°C to 800°C. The sintered bulk ceramics has a relative density as high as 95.5%. The dielectric and ferroelectric properties of the PZT ceramics are in good agreement with the widely reported results.

7.1.3 Coating of PZT composite thick films on Pt/Si substrate

By suspending PZT powder in PZT xerogel solution, uniform and stable slurry has been made that can be used to coat PZT composite thick films on the platinum coated silicon substrate. Organic vehicle has been chosen as dispersant to eliminate the particles as agglomeration. After annealed at 700°C for 30 minutes, the resultant PZT composite thick films have dense, uniform and compact microstructures. No structural aggregation due to the loading of powder has been observed. The grains in the film developed fully and have an average size of 30 nm. The relative permittivity, dielectric loss, remnant polarization and coercive field of a typical thick film are 1115, 0.009, 11.7 $\mu\text{C}/\text{cm}^2$ and 42.3 kV/cm, respectively. The relatively poor ferroelectric properties are ascribed to the loaded nano-sized PZT powder.

7.1.4 Optimization of the hybrid processing technology

Optimization of the hybrid sol-gel composite process for thick film deposition has been realized by isolating and controlling the individual parameters of slurry characters and coating process. Generally, a higher xerogel solute concentration leads to denser microstructure; micron-sized powder loaded films have porous microstructure and more large size pores than that loaded with nano-sized powder. Single layer coating thicknesses increase linearly with the increase of powder solution ratio and it is determined by the solution concentration and powder size as well. The lower vehicle content, the denser the microstructure of the film is. High temperature heat treatment can improve the electrical properties by increasing the grain size and crystallinity of films. Too high an annealing temperature, however, leads to the peeling off of the platinum bottom electrode from silicon substrate. Replacing Ti by TiO_2 as the adhesion layer between platinum and underlying layers is an effective

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approach to prevent the peeling under high temperature annealing. In addition to high temperature annealing, optimizing the loaded powder with submicron size or pre-heat treatment of powder at high temperature can produce larger grain size in films or increase the degree of crystallinity of the powder, and thus improve the electrical properties. Back filling with pure xerogel solution and application of cold isostatic pressing technique can also improve the microstructure and electrical properties of the PZT composite thick films.

7.1.5 Integrated MEMS type devices applications

This thesis has presented a new combination of silicon micromachining technique and PZT thick film to form miniature transducers for ultrasonic application. The processes developed in this research are beneficial for future research on PZT-based MEMS type devices. In the future, PZT composite thick films will develop niche market applications. Piezoelectric PZT composite thick films have been deposited on Pt/Ti/LTO/Si₃N₄/SiO₂/Si substrates. Square diaphragms ranging from 0.5 mm to 2 mm in dimension have been successfully fabricated, and phased transducer arrays with 2 to 5 rings have been realized. Deflection amplitude, frequency response, and acoustic transmitting properties have been investigated.

7.2 Recommendations

The results of our experiments leave to several questions for an answer. While our hybrid sol-gel composite process is well explored and provides suitable films for device applications, there are still some aspects we do not fully understand, or that can be further improved.

The process developed in this thesis for preparation of high quality PZT53/47 ferroelectric composite thick films, i.e., the hybrid sol-gel composite approach, can be

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used for other PZT compositions as well as other electroceramic (bulk or thick film) material systems, such as lead zinc niobate $[\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3]$ and lead magnesium niobate $[\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3]$. Issues that remain are possible further optimization of the derived PZT films to enhance ferroelectric and piezoelectric properties, so that it can result in a more flexible and versatile approach of material synthesis and processing for a wide variety of applications. For example, depositing films of uniform thickness throughout the wafer will become a priority because of the influence of film thickness on the operation characteristics of MEMS devices. It is of great importance to produce acceptable devices in batch production. Quantitative evaluation of the effect of slurry characters on films properties, such as solvent and slurry viscosity should also be carried out in more details.

The direct amorphous to perovskite phase transformation pathway has been suggested through the study of xerogel precursor. This direct transformation is important for the ferroelectric film integration into the Si micromachining technology, since the undesirable, non-ferroelectric pyrochlore phases is possible to be eliminated completely. The transformation observed in this thesis has wider applications on perovskite, lead based ferroelectric material systems such as PZT, PMN, PZN, where the pyrochlore phases are generally considered as a intermediate stage of phase development. Further work should include the studies on phase transformation kinetics and transformation sequence of these systems.

The properties of the PZT thick films, such as Young's modulus and the unclamped piezoelectric constant, which are very important for piezoelectric applications, are not yet well understood. The Young's modulus of the PZT film could be calculated from the measured resonant frequency of the structure, after removing the entire silicon layer. Taking advantage of the microfabrication processing

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and measurement techniques developed in this thesis it could be studied in detail. Due to sensitivity of piezoelectric response in film piezoelectrics, however, enhanced stability and resolution will be beneficial for accurate characterization. A highly sensitive double beam laser interferometer system is supposed to accurately characterize the piezoelectric properties. A simple structure, such as cantilever beam or a diaphragm, would be preferred since analytical models of these structures would be helpful to extract material properties from the experimental data. The clamped piezoelectric constant as a function of the silicon thickness (or the ratio of the silicon and PZT layers) could be obtained by changing the thickness of the silicon and PZT layers. Based on the measured data, a theoretical model for the clamping effect could be derived.

A fair amount of work remains in fabricating MEMS type devices and optimizing their piezoelectric response. For example, we still have problems with our films uniformity, and patterning of PZT films. And the study shows that the composite PZT thick films have good potential applications in phased array for audio beam micro-loudspeaker application using the piezoelectric ultrasonic transducer diaphragm. With the knowledge of key material parameters, the response of phased array of piezoelectric ultrasonic transducers for air-used loudspeaker can be simulated using finite element analysis. This is a necessary step to gain insight into the design of audio beamed micron-loudspeaker and to be able to combine different materials and array geometries in order to produce the optimal device.

In summary, this thesis demonstrates not only a novel hybrid processing technology for PZT thick film deposition, but also opens a new field combining the piezoelectric films and silicon micromachining techniques for future MEMS type devices applications.

PUBLICATION LIST

Patents

1. W. G. Zhu, Z. H. Wang, C. L. Zhao and O. K. Tan, “Process for producing nanocrystalline composites by mixing organo-metallic precursor with nanosized powders”, filed on June 19,2002. Singapore patent application No 200203 154-0

Journal Papers

1. W. G. Zhu, Z. H. Wang, C. L. Zhao, O. K. Tan, “Low Temperature Sintering of Piezoelectric Thick Films Derived from a Novel Sol-gel Route”, Japanese Journal of Applied Physics, Vol.41 (2002) No.11B
2. C. L. Zhao, Z. H. Wang, W. G. Zhu, X. Yao and W. G. Liu, “PZT thick films fabrication using a sol-gel based 0-3 composite processing”, Inter. J. Mod. Phys.B, 16:242~48(2002)
3. C. L. Zhao, Z. H. Wang, W. G. Zhu, O. K. Tan and H. H. Hng, “Microstructure and properties of PZT53/47 thick films derived from sols with submicron-sized PZT particle”, Ceramics International 30: 1925~27(2004)
4. Z. H. Wang, W. G. Zhu, C. L. Zhao and O. K. Tan, “Dense PZT thick films derived from sol-gel based nanocomposite process” Materials and Engineering B: Solid State Materials for Advanced Technology, 99 (1-3): 56-62(2003)

Publication list

5. Z. H. Wang, C. L. Zhao, W. G. Zhu, O. K. Tan, W. G. Liu and X. Yao, “Processing and Characterization of Pb(Zr,Ti)O₃ Thick Film on Platinum-Coated Silicon Substrate Derived from Sol-Gel Casting”, Materials Chemistry and Physics, 75(1-3), 2002, 71-75
6. Z. H. Wang, W. G. Zhu, C. Chao, C. L. Zhao and X. F. Chen, “Characterization of composite piezoelectric thick film for MEMS applications”, Surface and Coatings Technology, accepted
7. Z. H. Wang, W. G. Zhu, J. Miao, C. Chao, C. L. Zhao and O. K. Tan, “Fabrication and characterization of piezoelectric micromachined ultrasonic transducers with thick composite PZT films”, IEEE Transaction on Ultrasonics, Ferroelectrics, and Frequency Control, accepted
8. Z. H. Wang, W. G. Zhu, C. L. Zhao and X. Yao, “Deflection Characteristics of a Trapezoidal Multilayer Inplane Bending Piezoelectric Actuator”, IEEE Transaction on Ultrasonics, Ferroelectrics, and Frequency Control, 48(4), 2001, 1103-1110

Conference Papers

1. C. L. Zhao, Z. H. Wang, W. G. Zhu and O. K. Tan, “Sol-gel Derived PZT Thick Films for Fabrication of Piezoelectric Diaphragm”, Fall Meeting, MRS2002
2. Z. H. Wang, C. L. Zhao, W. G. Zhu, O. K. Tan, and X. F. Chen, “Piezoelectric thick films for microelectromechanical system applications”, 1st International Conference on Materials Processing for Properties and Performance, 1-3 August, 2002, Singapore

Publication list

3. Z. H. Wang, W. G. Zhu, C. L. Zhao, H. Zhu and J. M. Miao, “Piezoelectric microactuator arrays using composite PZT thick films”, AMEC-3, Singapore, 2003
4. Z. Wang, W. Zhu, O. K. Tan, C. L. Zhao, H. Zhu and J. Miao, “MEMS device arrays using thick composite PZT films”, ACS 106th Annual Meeting & Exposition, April 18-21, 2004, Indian, USA
5. Z. Wang, W. Zhu, C. Zhao, C. Chao, H. Zhu, and J. Miao, “MEMS Device Arrays Using Thick Composite PZT films”, 106 Am. Ceram. Soc. Meeting, 2003

BIBLIOGRAPHY

- [1] D. S. Eddy, and D. R. Sparks, "Applications of MEMS technology in automotive sensors and actuators", Proc. of the IEEE, V86[8]: 1747–55, 1998
- [2] M. Mollendorf, "Micro-electro-mechanical-systems and industrial applications", Proc. of ASME Aerospace Division, V52: 761–67, 1996
- [3] D. L. Polla, "Ferroelectric microsensors and microactuators" Proc. 8th IEEE int. Symp. On Application of Ferroelectrics, p127 (1992)
- [4] D. L. Polla, C. Ye and T. Tamagawa, "Surface micromachining of PbTiO₃ pyroelectric detectors" Appl. Phys. Lett., 59: 3539(1991)
- [5] M. Sayer, "Integrated piezoelectric and pyroelectric devices from thin film ferroelectrics", Mater. Res. Soc.: 2001 Fall meeting, Boston, Dec 2001
- [6] P. Schiller, C. Ye, T. Tamagawa and D. L. Polla, "Design and process considerations for ferroelectric film-based piezoelectric pressure sensors", 4th Inte. Symp. on Integ. Ferroelec., Monterey, Mar 1992
- [7] S. B. Krupanidhi and M. Sayer, "Radio frequency magnetron sputtering of multicomponent ferroelectric oxides", J. Vac. Sci. Tech., A2: 303(1984)
- [8] D. Roy, S. B. Krupanidhi and J. Dougherty, "Excimer laser ablated lead zirconate titanate thin films", J. Appl. Phys., 69(11): 7930(1991)
- [9] S. Mansour, G. Liedl, R. Vest, "Microstructural Developments and Dielectric Properties of Rapid Thermally Processed PZT Thin Films Derived by Metallo-organic Decomposition", J. Am. Ceram. Soc. 78, 1617(1995)
- [10] T. R. Shrout and S. L. Swartz, "Processing of Ferroelectric and Related Materials: A Review"; Proceedings of the 8th IEEE International Symposium on Applications of Ferroelectrics. IEEE, Piscataway, N.J., 80-88(1992)
- [11] B. Noheda, D. E. Cox, G. Shirane, R. Guo, B. Jones, and L. E. Cross, "Stability of the monoclinic phase in the ferroelectric perovskite PbZr_{1-x}Ti_xO₃", Phys. Rev. B., V63: 014103, 2001
- [12] L. Bellaiche, A. Garcia, and D. Vanderbilt, "Finite-temperature properties of PZT alloys from first principles", Phys., Rev. B. Lett., V84: 5427, 2000
- [13] A. G. Sonze Filho, K. C. V. Lima, A. P. Ayala, I. Guedes, P. T. C. Freire, J. Mendes Filho, E. B. Araujo, and J. A. Eiras, Phys. Rev. B., V61: 14283, 2000
- [14] Gerson, R., "Variation in Ferroelectric Characteristics of Lead Zirconate Titanate Ceramics" J. Appl. Phys., V31 [1]: 188-194, 1960
- [15] Martrena, H. T., and Burfoot, J. C., "Grain Size Effects on Properties of Some Ferroelectric", J. Phys. C: Solid State Phys., V7: 3182-3192 (1974).
- [16] Mishra, S. K. and Pandey, D., "Effect of Particle Size on the Ferroelectric Behaviour of Tetragonal and Rhombohedral Pb(Zr_xTi_{1-x})O₃ Ceramics and Powders", J. Phys.: Condens. Matter, V7, 9287-9303 (1995)

Bibliography

- [17] Ogawa, T., "High Functional and High-performance Piezoelectric Ceramics", *Am. Ceram. Bull.*, V70 [4]: 1042-1049(1991).
- [18] Kim, S., Lee, G. S., Shrout, T. R. and Venkataramani, S., "Fabrication of Fine-Grain Piezoelectric Ceramics Using Reactive Calcination", *J. Mater. Sci.*, V26: 4411-4415 (1991).
- [19] Zhang, X. L., Chen, Z. X., Cross, L. E., and Schulze, W. A., "Dielectric and Piezoelectric Properties of Modified Lead Titanate Zirconate Ceramics from 4.4 K to 300 K", *J. Mater. Sci.*, V18 [4]: 968-972 (1983).
- [20] B. Jaffe, William, R. Cook, and H. Jaffe, *Piezoelectric Ceramics* (Academic Press, London, 1971)
- [21] K. Lefki and G. J. M. Dormans, "Measurement of piezoelectric coefficients of ferroelectric thin films", *J. Appl. Phys.*, V76: 1764(1994)
- [22] S. Trolier-McKinstry, J. F. Shepard, Jr., T. Su, J. L. Lacey, G. Zavala, and J. Fendler, "Piezoelectricity in Ferroelectric Thin Films: Domain and Stress Issues", *Ferroelectrics*, V206: 381(1997)
- [23] F. Xu, S. Trolier-McKinstry, W. Ren, B. Xu, Z. L. Xie, and K. J. Hemker, "Domain wall motion and its contribution to the dielectric and piezoelectric properties of lead zirconate titanate films", *J. Appl. Phys.*, V89: 1336(2001)
- [24] S. Hiboux, P. Muralt, and T. Maeder, "Domain and lattice contributions to dielectric and piezoelectric properties of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ thin films as a function of composition", *J. Mater. Res.*, V14: 4307(1999)
- [25] H. D. Chen, K. R. Udayakumar, C. J. Gaskey, and L. E. Cross, "Electrical properties' maxima in thin films of the lead zirconate-lead titanate solid solution system", *Appl. Phys. Lett.*, V67: 3411(1995)
- [26] G. Teowee, K. C. McCarthy, F. S. McCarthy, D. G. Davis, Jr., J. T. Dawley, B. J. J. Zelinski, and D. R. Uhlmann, *Mat. Res. Soc. Symp. Proc.*, V493: 439, (1998)
- [27] D. V. Taylor and D. Darnvanovic, *Appl. Phys. Lett.*, V76: 1615(2000)
- [28] S. Hiboux, P. Muralt, and N. Setter, *Mat. Res. Soc. Symp. Proc.*, V596: 499, (2000)
- [29] T. Sokoda, K. Aoki, and Y. Fukuda, "Characteristics of sputtered PZt thin films with various compositions", *Jpn. J. Appl. Phys.*, V38[1]: 3600~03(1999)
- [30] M. Sayer and Sreenivas, K., "Ceramic thin films: fabrication and application", *Science*, V247: 1056(1990)
- [31] S. P. Beeby, A. Blackburn, and N. M. White, "Silicon micromachining processes combined with thick-film printed lead zirconate titanate actuators for microelectromechanical system", *Mater. Lett.*, V40: 187-91(1999)
- [32] S. P. Beeby, A. Blackburn, and N. M. White, "Processing of PZT piezoelectric thick films on silicon for microelectromechanical systems", *J. Micromech. Microeng.*, V9[3]: 218~29(1999)
- [33] H. D. Chen, K. R. Udayakumar, L. E. Cross, J. J. Bernstein and L. C. Niles, "Development and electrical characterization of lead zirconate titanate thick films on silicon substrates", *IEEE*, 495(1995)

Bibliography

-
- [34] U. Selvaraj, K. Brooks, A. V. Prasadaraio, S. Komameni, R. Roy and L. E. Cross, "Studies of substrate materials for PZT thin films" J. Am. Cera. Soc., 76[6]: 1441(1993)
 - [35] S. Chen and I. Xhen, "Temperature-time texture transition of $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ thin films: I, role of Pb-rich intermediate phases" J. Am. Cera. Soc., 77[9]: 2332(1994)
 - [36] D. Sporn, S. Merklein, W. Grond, S. Seifert, S. Wahl and A. Berger, "Sol-gel processing of perovskite thin films" Microelec. Eng., 29: 161(1995)
 - [37] M. Lukacs, M. Sayer and S. Foster, "Single element high frequency (<50 MHz) PZT sol gel composite ultrasound transducers" IEEE Trans. On Ultrasonics, Ferroelectrics, and Frequency Control, 47[1]: 148(2000)
 - [38] G. Yi and M. Sayer, "Sol-gel processing of complex oxide films" Cera. Bull., 70: 1173(1991)
 - [39] S. J. Milne and S. H. Pyke, "Modified sol-gel process for the production of lead titanate films", J. Am. Cera. Soc. 74[6]: 1407(1991)
 - [40] S. D. Ramamuthi and D. A. Payne, "Structure investigations of prehydrolyzed precursors used in the sol-gel processing of lead titanate" J. Am. Cera. Soc., 73[8]: 2547(1990)
 - [41] C. Lakeman and D. A. Payne, "Processing effects in the sol-gel preparation of PZT dries gels, powders, and ferroelectric thin layers" J. Am. Cera. Soc., 75[11]: 3091(1992)
 - [42] A. Wu, P. M. Vilarinho, I. Salvado and J. Baptista, "Sol-gel preparation of lead zirconate titanate powders and ceramics: effect of alkoixde stabilizers and lead precursors" J. Am. Cera. Soc., 83[6]: 1379(2000)
 - [43] Y. Takahashi, Y. Matsuoka, K. Yamaguchi, M. Matsuki and K. Kobayashi, "Dip coating of PT, PZ and PZT films using an alkoxide-diethanolamine method" J. Mater. Sic., 25: 3960(1990)
 - [44] G. Yi, Z. Wu and M. Sayer, "Preparation of $\text{Pb}(\text{Zr,Ti})\text{O}_3$ thin films by sol gel processing: Electrical, optical, and electro-optic properties", J. Appl. Phys., 64: 2717(1988)
 - [45] A. H. Carim, B. A. Tuttle, D. H. Doughty and S. L. Martinez, "Microstructure of solution-processed lead zirconate titanate (PZT) thin films" J. Am. Cera. Soc., 74[6]: 1455(1991)
 - [46] G. M. Spierings, M. Ulenaers, G. Kampschoer, H. Hao and P. K. Larsen, "Preparation and ferroelectric properties of $\text{PbZr}_{0.53}\text{Ti}_{0.47}\text{O}_3$ thin films by spin coating and metalorganic decomposition" J. Appl. Lett., 63[2]: 153(1993)
 - [47] M. Klee, R. Eusemann, R. Waster, W. Brand and H. Hao, "Processing and electrical properties of $\text{Pb}(\text{ZrxTi}_{1-x})\text{O}_3$ ($x = 0.2-0.75$) films: comparison of metallo-organic decomposition and sol-gel processes" J. Appl. Phys., 72[4]: 1566(1992)
 - [48] G. Yi, Z. Wu, M. Sayer, C. Jen and J. F. Bussiere, "Sol-gel processed piezoelectric PZT thin films" Cera. Trans., 11: 363
 - [49] A. Tanaka, S. C. Chov, M. Miyayama, A. Bhalla and H. Yanagida, "Studies of substrate materials for PZT thin films", Inte. Ferroelec., 3: 51(1993)

Bibliography

-
- [50] P. Tan, T. Su, L. T. Li and X. W. Zhang, "Preparation and characterization of sol-gel derived PZT bulk ceramics and thin films" *Functional Mater.*, 26[2]: 131(1995)
 - [51] D. Sporn, S. Merklein, W. Grond, S. Seifert, S. Wahl and A. Berger, "Sol-gel processing of perovskite thin films", *Microelec. Eng.*, 29: 161(1995)
 - [52] Y. L. Tu, M. L. Calzada, N. J. Philips and J. Milne, "Synthesis and electrical characterization of thin films of PT and PZT made from a diol-based sol-gel route" *J. Am. Cera. Soc.*, 79[2]: 441(1996)
 - [53] Y. L. Tu and S. J. Milne, "Processing and characterization of Pb(Zr,Ti)O₃ films, up to 10 um thick, produced from a diol sol-gel route" *J. Mater. Res.* 11[10]: 556(1996)
 - [54] B. J. Kim, J. C. Lee, J. B. Yoo and K. S. No, "Pb(Zr,Ti)O₃ films fabrication by sol-gel method for piezoelectric actuated device" *Ferroelectrics*, 232: 247(1999)
 - [55] N. Sriprang, D. Kaewchinda, J. Kennedy and S. J. Milne, "Processing and sol chemistry of a triol-based sol-gel route for preparing lead zirconate titanate thin films" *J. Am. Cera. Soc.*, 83[8]: 1914(2000)
 - [56] W. G. Liu, W. G. Zhu and O.K. Tan, "Preparation on PZT thin films by a solid precursor sol-gel routine" 187(2000)
 - [57] J. Fukushima, K. Koaira and T. Matsushita, "Preparation of ferroelectric thin films by thermal decomposition of organometallic compounds" *J. Mater. Soc.*, 19: 595(1984)
 - [58] N. J. Philips, M. L. Calzada and S. J. Milne, "Sol-gel derived lead titanate films" *J. Non-crystal. Solids*, 147-148: 255(1992)
 - [59] H. Hu, L. Shi, V. Kumar and S. B. Krupanidhi, "Ferroelectric films" *Cera. Transc.*, 113 (1992)
 - [60] K. G. Brooks, I. M. Really, R. Klissurska, Y. Huang, C. Bursill and N. Setter, *J. Mater. Res.*, 9: 25(1994)
 - [61] C. J. Brinker, A. J. Hurd, P. R. Schunk, G. C. Frye and C. S. Ashiley, "Review of sol-gel thin film formation" *J. Non-crystal. Solid*, 147-148: 424 (1992)
 - [62] D. L. Polla, C. Ye and T. Tamagawa, "Surface micromachining of PbTiO₃ pyroelectric detectors" *Appl. Phys. Lett.*, 59: 3539(1991)
 - [63] G. Yi and M. Sayer, "Sol-gel processing of thick PZT films" *Pro. 8th IEEE Int. Symp. on Appl. of Ferroelec.*, 289(1992)
 - [64] R. H. Brazesowsky, G. de With, S. Cruijssem, I. Snikershendrickx, W. Wolter and J. G. Lierop, "Glass Strengthening by silica particle reinforced organic-inorganic coatings" *J. Non-crystal. Solids*, 241: 27(1998)
 - [65] D. A. Barrow, T. E. Petroff and M. Sayer, "Thick ceramic coatings using a sol-gel based ceramic-ceramic 0-3 composite", *Surface and Coating Tech.*, 76-77: 113(1995)
 - [66] S. M. Sze, *Semiconductor Sensors*, John Wiley & Sons, Inc.(1994)
 - [67] C. Lee, T. Itoh, and T. Suga, "Micromachined piezoelectric force sensors based on PZT thin films", *IEEE Trans. on UFFC*, V43[4]: 553(1996)

Bibliography

-
- [68] D. L. Polla, C. Ye, P. Schiller, T. Tamagawa, W. P. Robbins, D. Glumac, and C. C. Hsueh, "Applications of PZT and related thin films in piezoelectric microsensors", *Mater. Res. Soc. Symp. Proc.*, V243: 55(1992)
 - [69] W. Benecke, "Micromechanical sensors", *CompEuro'89*, "VLSI and computer peripherals. VLSI and microelectronic applications in intelligent peripherals and their interconnection networks", *Proc.* 1989
 - [70] W. P. Robbins, D. L. Polla, T. Tamagawa, D. E. Glumac, and W. Tjhen, "Design of linear-motion microactuators using piezoelectric thin films", *IEEE/ASME, J. MEMS*, V1: 247(1991)
 - [71] A. M. Flynn, L. S. Tavrow, S. F. Bart, R. A. Brooks, D. J. Ehrich, K. R. Udayakumar, L. E. Cross, "Piezoelectric micromotors for microrobots", *IEEE/ASME, J. MEMS*, V1: 44(1991)
 - [72] J. G. Smits, "Piezoelectric micropump with three valves working peristaltically", *Sensors and Actuators*, VA21–A23: 203(1990)
 - [73] T. Tsuchiya, T. Itoh, G. Sasaki and T. Suga, "Preparation and properties of piezoelectric lead zirconate titanate thin films for microsensors and microactuators by sol-gel processing", *J. Ceram. Soc. Jpn.*, V104[3]: 159(1996)
 - [74] I. Kanno, S. Fujii, T. Kamada, and R. Takayama, "Piezoelectric properties of C-axis oriented PZT thin films", *Appl. Phys. Lett.*, V70[11]: 1378(1997)
 - [75] K. R. Udayakumar, S. F. Bart, A. M. Flynn, J. Chen, L. S. Tavrow, L. E. Cross, R. A. Brooks, and D. J. Ehrlich, "Ferroelectric thin film ultrasonic micromotors", *Proc. IEEE Micro Electro Mechanical Systems*, Nara, Japan, 109(1991)
 - [76] J. F. Li, D. D. Viehland, T. Tani, C. Lakeman, and D. Payne, "Piezoelectric properties of sol-gel-derived ferroelectric and antiferroelectric thin layers", *J. Appl. Phys.*, V75[1]: 442(1994)
 - [77] D. Damjanovic, K. G. Brooks, A. Kholkin, M. Kohli, T. Maeder, P. Muralt and N. Setter, "Properties of piezoelectric PZT thin films for microactuator applications", *Mater. Res. Soc. Symp. Proc.*, V360: 429(1995)
 - [78] W. Zhu, K. Yao, and Z. Zhang, "Design and fabrication of a novel piezoelectric multilayer actuator by thick-film screen printing technology", *Sensors and Actuators A*, 86[3]: 149(2000)
 - [79] H. D. Chen, K. R. Udayakumar, C. J. Gaskey and L. E. Cross, "Fabrication and electrical properties of PZT thick films", *J. Am. Ceram. Soc.*, V79[8]: 2189(1996)
 - [80] T. Yamamoto, K. Okazaki, M. L. Dass and G. Thomas, "Microstructure and dielectric properties at the morphotropic phase boundary (MPB) of PbTiO₃-PbZrO₃ system", *Ferroelectric*, V81: 3319(1988)
 - [81] W. G. Liu, W. G. Zhu and O. K. Tan, "Preparation on PZT thin films by a solid precursor sol-gel routine", 187–190(2000)
 - [82] P. P. Phule, "Molecularly modified alkoxide precursors (MMAP) for thin film ferroelectric", *Proceedings of the international symposium on integrated ferroelectrics*, p118, 1992.

Bibliography

- [83] S. Doeuff, M. Henry, C. Sanchez and J. Livage, *J. Non-crystal. Solids*, 89: 206(1987)
- [84] D. L. Polla, W. P. Robbins, T. Tamagawa and C. Ye, "Ferroelectric thin films for microelectromechanical device application", *Mate. Res. Soc. Symp. Proc.*, 276: 3(1992)
- [85] R. Abothu, Y. Ito, P. Poosanaas, S. Kalalpat, S. Komarneni and K. Uchino, "Sol-gel processing of piezoelectric thin films" *Ferroelectrics*, 232: 191(1999)
- [86] Berlincourt, D., "Piezoelectric Ceramic Compositional Development", *J. Acoust. Soc. Am.*, V91[5]: 3034-3040, 1992
- [87] Xu, Y.; pp. 101-210 in *Ferroelectric Materials and Their Applications*, North Holland, 1991
- [88] B. A. Tuttle, T. J. Headley, B. C. Bunker, R. W. Schwartz, T. Zender, C. L. Hernandez, D. C. Goodnow, R. J. Tissot, J. Michael and A. H. Carim, "Microstructural evolution of Pb(Zr,Ti)O₃ thin films prepared by hybrid metallo-organic decomposition", *J. Mater. Res.*, V7: 1876, 1992
- [89] C. D. E. Lakeman, Z. Xu and D. A. Payne, "On the evolution of structure and composition in sol-gel-derived lead zirconate titanate thin layers", *J. Mater. Res.*, V10: 2042, 1995
- [90] C. K. Kwok and S. B. Desu, "Low temperature perovskite formation of lead zirconate titanate thin film by a seeding process", *J. Mater. Res.*, V8: 339, 1993
- [91] R. D. Klissurska, "Effect of Nb doping on the microstructure of sol-gel-derived PZT thin films", *J. Am. Ceram. Soc.*, V78: 1513–20, 1995
- [92] H. X. Zhang, S. Leppavuori, A. Uusimaki, P. Karjalainen and R. Rautioaho, in *Proceedings of the 8th International Meeting on Ferroelectricity*, 1995
- [93] C. A. Randall, N. Kim, J. P. Kucera, W. Cao and T. R. Shrout, *J. Am. Ceram. Soc.*, V81: 677, 1998
- [94] C. Jovalekic, M. Zdujic, A. Radakovic and M. Mitric, *Mater. Lett.*, V24: 365, 1995
- [95] H. D. Chen, K. R. Udayakumar, C. J. Gaskey, L. E. Cross, J. J. Brnstin and L. C. Nils, *J. Am. Ceram. Soc.*, V79: 2189, 1996
- [96] R. Kurchania and S. Milne, *J. Mater. Res.*, V14: 1852, 1999
- [97] M. Kosec, J. Holc, B. Malic and V. Bonbar, *J. Eur. Ceram. Soc.*, V19: 949, 1998
- [98] M. Sayer, M. Luckas, G. Pang, L. Zou, Y. Chen and J. Ken, *NATO Adv. Res. Workshaop on Piezoelectric Materials*, Predal, Rumania, 24-27, 1999
- [99] K. Shimomura, T. Tsurumi, Y. Ohba and M. Daimon, *Jap. J. Appl. Phys.*, V30: 2174, 1991
- [100] T. Ohno, M. Kunieda, H. Suzuki and T. Hayashi, *Jpn. J. Appl. Phys.*, V41: 6969, 2002

Bibliography

- [101] D. P. Birnie, "Rational solvent selection strategies to combat striation formation during spin coating of thin films", *J. Mater. Res.*, V16[4]: 1145(2001)
- [102] Y. Hirata and T. Ozaki, "Rheology and Consolidation of Aqueous Suspension with Nanometer-Sized BaTi_{1-x}ZrO_xO₃ Powders", *Mater. Lett.*, 15, 31-34 (1992).
- [103] J. Wen, G. Tomandl and A. Stiegelschmitt, "Electrophoretic Mobility in Ceramic Suspensions: Influence on Sintering Behaviour"; pp. 325-329 in *Second Euro-Ceramics, Vol. 1, Basic Science and Processing of Ceramics*, Ed. by G. Ziegler and H. Hausner, Deutsche Keramische Gesellschaft e.v. (1991).
- [104] D A Barrow, T E Petroff, R P Tandon and M Sayer, "Characterization of thick lead zirconate titanate films fabricated using a new sol-gel based process", *J Appl Phys*, 81[2]: 876-81(1997)
- [105] S. K. Dey, "Sol-gel science and pre-MOCVD of dielectric perovskite films", *Ferroelectric thin films: synthesis and basic properties*, 1996
- [106] P. Muralt, T. Maeder, L. Sagalowica, S. Hiboux, S. Salese, D. Naumovic, R.G. Agostino, N. Xanthopoulos, H. J. Matieu, L. Patthey and E. L. Bullock, "Texture control of PbTiO₃ and Pb(Zr,Ti)O₃ thin films with TiO₂ seeding", *J. Appl. Phys.*, V83[7]: 3835(1998)
- [107] G. R. Fox, S. Trolier-McKinstry and S. B. Krupanidhi, "Pt/Ti/SiO₂/Si substrates", *J. Mater. Res.*, V10[6]: 1508(1995)
- [108] Y. Matsui, M. Hiratani, Y. Kumagai, H. Miura and Y. Fujisaki, "Thermal stability of Pt bottom electrodes for ferroelectric capacitors", *Jpn. J. Appl. Phys.*, V37[2-4B]: 465(1998)
- [109] L. F. Madsen, and L. Weaver, "Examination of barrier layers for lead zirconate titanate thin films", *J. Electronic Materials*, V21[1]: 93(1992)
- [110] R. D. Klissurska, T. Maeder, K. G. Brooks, and N. Setter, "Microstructure of PZT sol-gel films on Pt substrates with different adhesion layers", *Microelectronic Engineering*, V29: 287(1995)
- [111] T. Maeder, L. Sagalowicz, and P. Muralt, "Stabilized platinum electrodes for ferroelectric film deposition using Ti, Ta, and Zr adhesion layers", *J. J. Appl. Phys.*, V37[1-4A]: 2007(1998)
- [112] J. H. Kim, L. Wang, S. M. Zurn, L. Li, Y. S. Yoon, D. L. Polla, *Integ. Ferroelec.* 15: 325 (1997)
- [113] C. Lee, T. Itoh, T. Suga, *IEEE Trans. Ultrason. Ferroelec. Freq. Contr.* 43: 553 (1996)
- [114] J. J. Bernstein, S. L. Finberg, K. Houston, L. C. Niles, H. D. Chen, L. E. Cross, K. K. Li and K. Udayakumar, "Micromachined high frequency ferroelectric sonar transducers", *IEEE Trans. UFFC*, V44[5]: 960(1997)
- [115] D. L. Polla, L. F. Francis, "Ferroelectric thin films in microelectromechanical systems applications", *MRS Bull.* 21(7): 59(1996)
- [116] B. M. Xu, L. E. Cross and J. J. Bernstein, "Ferroelectric and antiferroelectric films for microelectromechanical systems applications", *Thin Solid Films*, V377-378: 712(2000)

Bibliography

-
- [117] S. S. Lee and R. M. White, "Piezoelectric cantilever microphone, microspeaker, and voltage-to-frequency converter", Proc. ASME Dynamic Systems and Control Division, **975(1994)**
 - [118] S. S. Lee and R. M. White, "Self-excited piezoelectric cantilever oscillators", Proc. Transducers'95, IEEE Eighth International Conference on Solid State Sensors and Actuators and Eurosensors IX. Stockholm, Sweden, **417(1995)**
 - [119] M. E. Motamedi and R. M. White, "Acoustic sensors", in Semiconductor sensors, edited by S. M. Sze (John Wiley and Sons, Inc., New York, **1994**), **97-151**
 - [120] D. L. Devoe and A. P. Pisano, "A fully surface-micromachined piezoelectric accelerometer", Proc. Transducers '97, IEEE Ninth International Conference on Solid State Sensors and Actuators, Chicago, IL, USA, **1205(1997)**
 - [121] P. L. Chen, R. S. Muller, R. D. Jolly et al., "Integrated silicon microbeam PI-FET accelerometer", IEEE Transactions on Electron Devices, **V29[1]: 27(1982)**
 - [122] D. L. Polla, P. J. Schiller and L. F. Francis, "Microelectromechanical systems using piezoelectric thin films", Proc. SPIE, **V2291: 108(1994)**
 - [123] W. A. Gradia and C. M. Fortunko, "NDE applications of air-coupled ultrasonic transducers", in Proc. IEEE Ultraosn. Symp. **V1: 697(1995)**
 - [124] R. Farlow and G. Hayward, "Real-time ultrasonic techniques suitable for implementing non-vol-contact NDT systems employing piezoceramic composite transducers", Insight, **V36[12]: 926(1994)**
 - [125] G. Hayward and A. Gachagan, "An evaluation of 1-3 connectivity composite transducers for air-coupled ultrasonic applications", J. Acoust. Soc. Amer., **V99[4]: 2148(1996)**
 - [126] R. C. Buchanan, "Ceramic materials for electronics: processing, properties, and applications", 2nd Edition, Marcel Dekker, Inc., New York (1991)
 - [127] A. M. Flynn, "Piezoelectric micromotors for microrobots", J. Microelectromech. Syst., **V1: 44(1992)**
 - [128] S. Watanabe, M. Suzuki and T. Fujiu, J. Vac. Sci. Technol. B, **V13: 1119, 1995**
 - [129] P. Lugienbuhl, et al., "Piezoelectric cantilever beams actuated by PZT sol-gel film", Sensors and Actuators A, **V53: 530(1996)**
 - [130] Y. Miyahara, et al., "PZT cantilever for non-contact atomic force microscopy", Appl. Surf. Sci., **V140: 428(1999)**
 - [131] P. Muralt, M. Kohli, T. Maeder, A. Kholkin, K. Brooks, N. Setter, R. Luthier, "Fabrication and characterization of PZT thin-film vibrators for micromotors", Sensors and Actuators **A, V48: 157(1995)**
 - [132] M. Dubois and P. Muralt, "PZT thin film actuated elastic fin micromotor", IEEE Trans. UFFC, **V45: 1169(1998)**
 - [133] P. Lugienbuhl, et al., "Microfabricated lamb wave device based on PZT sol-gel thin film for mechanical transport of solid particles and liquids", J. Micromech. Syst., **V6: 337(1997)**
 - [134] N. A. Riza, Electron. Lett., **V29: 1606(1993)**

Bibliography

- [135] Shuichi, W., Minoru S., Hiroshi, G, Masashi T and Tsuneji Y, “Static characteristic of piezoelectric thin film buckling actuator”, Jpn. J. Appl. Phys., 35: 5012 (1996)
- [136] Maxim Lebedev, Jun Akedo and Yoshikazu Akiyama, “Actuation properties of lead zirconate titanate thick films structured on Si membrane by the aerosol deposition method”, Jpn. J. Appl. Phys., Vol. 39: 5600-5603(2000)
- [137] Takaaki Tsurumi, Shuichi Ozawa, Goro Abe, Naoki Ohashi, Satoshi Wada and Masayuki Yamane, “Preparation of Pb(Zr_{0.53}Ti_{0.47})O₃ thick films by an interfacial polymerization method on silicon substrates and their electric and piezoelectric properties”, Jpn. J. Appl. Phys., Vol. 39: 5604 (2000)
- [138] G. R. Fox, S. Troler-Mckinstry and S. B. Krupanidhi, J. Mater. Res., V10(6): 1508(1995)
- [139] J. L. Vossen and W. Kern, “Thin film processes”, 1st ed., part V- 1 (Academic Press, New York, 1978)
- [140] W. Liu, J. Ko and W. Zhu, “Device patterning of PZT/Pt/Ti/Thin films on SiO₂/Si₃N₄ membrane by a chemical wet etching approach”, J. Mater. Sci. Lett., v19: 2263(2000)
- [141] I. Zubel and I. Barycka, “Silicon anisotropic etching in alkaline solutions I. The geometric description of figures developed under etching Si(100) in various solutions”, Sensors and Actuators A, V70: 250(1998)
- [142] I. Zubel, “Silicon anisotropic etching in alkaline solutions II One the influence of anisotropy on the smoothness of etched surfaces”, Sensors and Actuators A, V70: 260(1998)
- [143] I. Zubel, “Silicon anisotropic etching in alkaline solutions 111: On the possibility of spatial structures of forming in the course of Si(100) anisotropic etching in KOH and KOH + IPA solutions”, Sensors and Actuators A, V84: 116(2000)
- [144] I. Zubel, I. Barycka, K. Kotowska, M. Kramkowska, “Silicon anisotropic etching in alkaline solutions IV: The effect of organic and inorganic agents on silicon anisotropic etching processes”, Sensors and Actuators A, V87: 163(2001)
- [145] I. Barycka and I. Zubel, “Silicon anisotropic etching in KOH-isopropanol etchant”, Sensors and Actuators A, V48: 229(1995)
- [146] S. S. Beeby, A. Blackburn and N. M. White, “Processing of PZT piezoelectric thick films on silicon for microelectromechanical systems”, J. Micromech. Microeng. V9: 218(1999)
- [147] K. Saito, J. H. Choi, T. Fukuda and M. Ohue, Jpn. J. Applied Physics, V31: 1260(1992)
- [148] C. J. Kim, J. K. Lee, C. W. Chung, I. Chung, Integrated ferroelectrics proceedings of technology, V16(1-4): 149(1997)
- [149] S. Yokoyama, Y. Ito, K. Ishihara, K. Hamada, S. Ohnishi, J. Kudo and K. Sakiyama, Jpn. J. Applied Physics, V34: 767(1995)
- [150] L. P. Wang, R. Wolf, Q. Zhou, S. Troler-Mckinstry, and R. J. Davis, “Wet-etch patterning of lead zirconate titanate (PZT) thick films for

Bibliography

- microelectromechanical systems (MEMS) applications”, MRS Symp. Proc., V657(2001)
- [151] K. Yao and K Uchino, “Analysis on a composite cantilever beam coupling a piezoelectric bimorph to an elastic blade”, Sensors and Actuators A, V89: 215(2001)
- [152] R. Noble, A Jones, T. Roberson and D. Hutchins, “Novel, wide bandwidth, micromachined ultrasonic transducers”, IEEE Trans. on UFFC, V48[6]: 1495(2001)
- [153] K. Yamashita, H. Katata, M. Okuyama, H. Miyoshi, G. Kato, S. Aoyagi and Y. Suzuki, “Arrayed ultrasonic microsensors with high directivity for in-air use using PZT thin film on silicon diaphragms”, Sensors and Actuators A, V97-98: 302(2002)
- [154] C. L. Dym, I. H. shanmes, “Solid mechanics: a variational approach”, McGraw-hill, New York, 1973
- [155] D. Young, “Vibration of rectangular plates by the ritz method”, J. Appl. Mech., V17: 448(1950)
- [156] R.D. Blevins, “Formulas for natural frequency and mode shape”, Malabar, FL: Krieger Publishing Co., 1995
- [157] P. Muralt, A. Kholkin, M. Kohli and T. Maeder, “Piezoelectric actuation of PZT thin film diaphragms at static and resonant conditions”, Sensors and Actuators A, V53:397(1996)
- [158] P. Gaucher, “Piezoelectric micro-electro-mechanical systems for acoustic applications”, Workshop “Piezoelectric for the End User”, Interlaken, Feb 25-27, 2002 ., in “Piezoelectric Materials and Devices”, ed N. Setter, May 2002
- [159] G. Percin, A. Atalar, F. L. Degertekin, and B. T. Khuri-Yakub, “Micromachined two dimensional array piezoelectrically actuated transducers”, Appl. Phys. Lett., V72: 1397(1998)
- [160] I. Ladabaum, A. Atalar, C. Quate, and B. Khuri-Yakub, “Silicon micromachined ultrasonic immersion transducers”, App. Phys. Lett. V69: 3674(1998)
- [161] G. Lindstedt and G. Olsson, “Using low cost piezoelectric ultrasonic sensors for 3D measurement in robots”, Low Cost Automation 1992. Techniques, Components and Instruments, Applications, Selected papers from the 3rd IFAC Synmposium, 1993: 35–40
- [162] S. C. Wooh and Y. Shi, “Influence of phased array element size on beam steering behavior”, Ultrasonic V36: 737(1998)
- [163] S. C. Wooh and Y. Shi, “Optimization of ultrasonic phased array”, Rev. Prog. Quant. Nondestructive Eval. V1[2]: 883(1998)
- [164] M. Maekawa, A. Jitsumori and T. Inari, “Two dimensional ultrasonic scanning method using a circuit-array transducer”, Jpn. J. Appl. Phys., V25(Suppl. 25-1): 85(1986)
- [165] W. D. Kingery, H. K. bowen and D. R. Uhlmann, “Introduction to ceramics”, Wiley, New York, 1976

APPENDIX: PHOTO MASKS FOR PHASED ARRAY FABRICATION

#1. Bottom electrode coating

#2. Backside silicon wet etching

Appendix. Photo masks for phased array fabrication

#3. PZT wet etching

#4. Polyimide patterning.

#5. Top electrode coating.

Overview of the overlapped 5 layers photo mask.