Piezoelectric films using hybrid technology for ultrasonic array and electronic device applications

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Piezoelectric Films Using Hybrid Technology for Ultrasonic Array and Electronic Device Applications

Chao Chen

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

2005

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

Date

Chao Chen

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SUMMARY

Lead zirconate titanate (PZT) films are promising for MEMS type micro-devices applications because of their high electromechanical coupling coefficients and excellent piezoelectric properties. PZT piezoelectric film integrated on silicon substrate for various MEMS devices has been the subject of considerable attention in recent years. In this thesis, a broad range of work is presented, including the deposition of PZT films onto silicon substrates, the development of a novel interferometric system and related method for piezoelectric characterization of PZT films, as well as the design and fabrication of diaphragm-type piezoelectric micromachined ultrasonic transducer arrays.

Three kinds of sol-gel routes are studied. Some related kinetic parameters of phase formation are calculated using Kissinger's method. A PZT thin film deposition method is developed based on a modified acetic acid route, enabling PZT thin films with thickness less than 2 microns to be deposited on silicon substrate. A hybrid deposition technique is presented. PZT thick films ranging from several microns to 20 microns are successfully fabricated onto silicon substrate. Phase formation, microstructure, dielectric and ferroelectric properties for these PZT thin/thick films are characterized.

In the development of a high-sensitivity interferometric method for piezoelectric characterization, a modulation technique has been proposed and realized to overcome the random drift problem of the fringes caused by the environment or even the intensity variation of the laser source. An ultrahigh out-of-plane displacement

Summary

resolution down to pico meter required for piezoelectric characterization of thin films is achieved. Based on the modulation technique, a high-resolution scanning homodyne interferometer is successfully developed for characterization of piezoelectric thin films as well as for vibration measurement of MEMS devices.

By employing the novel scanning characterization technique, some piezoelectric thin/thick film samples are characterized with enhanced accuracy and consistency compared with single point measurements. The effect of several processing parameters, i.e., sol-gel concentration, powder-to-solution ratio and cold isostatic pressing on the piezoelectric properties of the resultant PZT films is also discussed.

New types of piezoelectric pMUT arrays for ultrasonic transmitter application are successfully developed based on the combination of silicon micromachining technology and hybrid PZT film deposition technology. Design issues and fabrication processes are discussed in details. Square or rectangular diaphragms with size ranging from 0.1 mm to 2 mm are fabricated. The elements are arranged to form different types of ring arrays and linear arrays. The performance of the prototype devices are investigated in terms of membrane deflection, emitting sound pressure, and directivity of emitting ultrasound beam. The resonance frequency dependence on the element size and the dc bias are discussed. High output SPL and desirable directivity patterns are achieved.

CHAPTER ONE

INTRODUCTION

1.1 Motivation

Microelectromechanical systems (MEMS) are currently viewed as providing enormous opportunities for perceiving and controlling a variety of physical environments. A wide variety of MEMS devices including sensors, actuators, and micro-optical components have been demonstrated based on numerous electro-mechanical coupling mechanisms, such as electro-static, electro-magnetic, electro-thermal, piezoelectric mechanisms, etc. Electro-static MEMS is the most frequently used form of actuation due to its modest actuation voltages, general simplicity, and relatively low cost to implement. In addition, the optimum geometry necessary for electrostatic actuation is also suitable for capacitive sensing. In comparison with electro-static mechanism, piezoelectric actuation provides more direct electro-mechanical coupling with higher dynamic response and larger force. Furthermore, piezoelectric MEMS usually possess much simpler structures. From the point view of

reliability, simpler structures are preferred because they are generally less subject to failure problem. However, due to the difficulty in deposition of thick PZT film, piezoelectric MEMS have not been investigated sufficiently. Although some promising device designs have been proposed, successfully fabricated prototypes are still very few. The development of processing for fabrication of piezoelectric MEMS is still a challenging work.

The development of piezoelectric MEMS requires a number of piezoelectric materials being integrated on silicon substrate for micromachining. Among these materials, lead zirconate titanate ($\text{Pb}(\text{Zr,Ti})\text{O}_3$) is the most prominent for its high piezoelectric properties, but leaves a technical challenge of film deposition on Si substrate. Due to its advantage on stoichiometric control, sol-gel coating technology is regarded as a suitable method for deposition of multi-component materials such as PZT on silicon substrate. Moreover, sol-gel method possesses some other advantages such as low initial processing temperature, high purity, and low cost. High quality, crack-free, homogeneous PZT thin films with thickness less than 1 μm have been successfully prepared using sol-gel method. The films serve well for sensing applications. When it comes to actuating applications, thicker films (1~50 μm in thickness) are required to generate both higher force and larger displacement. This thickness range is also of particular interest for high-frequency ultrasonic imaging. However, the fabrication of PZT films within thickness range of 1~50 μm has long been a technical difficulty. For currently established sol-gel techniques, the critical thickness is usually limited to around 1 μm , beyond which cracking occurs. Furthermore, the deposited thin films often possess defects such as pin holes, which lead to electrical breakdown and low yield of the fabricated devices. Therefore, development of modified deposition

techniques is quite essential to increase the film thickness as well as to improve the film quality.

The application of piezoelectric thin/thick films on silicon substrate for various MEMS devices requires intensive investigation of piezoelectric properties in thin films. With the thickness shrinking to the magnitude of microns, the piezoelectric performance of the thin film material is increasingly dependent on various factors such as the film orientation, cavity or defect density, substrate constraint and film thickness itself. The effective piezoelectric properties for thin films may exhibit a difference from those of bulk materials. Much work has been done on the piezoelectric coefficient measurement of thin films and a number of innovative techniques have been established. However, discrepancy among the reported data in the literature is significantly large, suggesting many of the measurement techniques might not be accurate or reliable. There is an urgent need to develop a widely accepted standard method for piezoelectric characterization of thin films.

Ultrasonic technologies have been widely used for the distance recognition, biomedical-imaging and automotive sensing applications. Its non-destructive nature enables the technique to be used for *in vivo* imaging of tissues, and aids much of its clinical acceptance. In recent years, there is, particularly in the case of ultrasonic imaging for medical diagnosis, an evident technological trend towards further miniature of device size and higher operating frequencies in order to achieve higher axial or lateral imaging resolution. The conventional technology based on bulk piezoelectric ceramic transducers becomes increasingly difficult to meet the requirements. Piezoelectric micromachined ultrasonic transducers (pMUTs) represent

a promising approach to ultrasound detection and generation in replacement of conventional ceramic transducers. As a kind of piezoelectric MEMS devices, pMUTs offer advantages of easy fabrication of large arrays with compact designs and integration with support electronics. These advantages, inherent in pMUTs, enable revolutionary advances in ultrasonic imaging and many other promising applications, such as acoustic devices, low cost phase arrays in distance measurement, and ultrasonic imaging.

1.2 Objectives

In this thesis, the final goal is to fabricate diaphragm-type piezoelectric micromachined ultrasonic transducer (pMUT) arrays for directional ultrasound radiating applications. The project includes the development of deposition techniques of thin/thick piezoelectric films on silicon substrate as well as the design and fabrication of prototype MEMS by combining the established film deposition technology with silicon micromachining technology.

Aiming at this purpose, the works are directed towards the following objectives:

1. Development of a suitable route for sol-gel deposition of PZT thin films on silicon substrate;
2. Deposition of dense, crack-free PZT thin films with desired thickness range (1~2 μm) and optimized ferroelectric properties;

3. Thick film (3~20 μm) deposition by a sol-gel based ceramic-ceramic 0-3 composite coating technique;
4. Establishment of a displacement measuring tool (interferometric system) with reliability and high resolution (10^{-2} Å) for piezoelectric characterization of the PZT thin/thick films;
5. Design and fabrication of prototype devices using the PZT film deposition technology and silicon micromachining technology.

1.3 Major Contributions of the Thesis

The major contributions achieved in the thesis are summarized as follows:

1. A study of sol-gel routes has been carried out to provide detailed information about the phase formation process during PZT thin film fabrication. The crystallization kinetics is investigated by thermal analysis methods. Key kinetic parameters of phase formation during film firing are calculated using Kissinger's method.
2. PZT (53/47) thin films with thickness ranging from 0.5~1.1 μm have been deposited by using acetic acid sol-gel method on silicon substrate. With a modified acetic acid sol-gel route, uniform, dense films with a single layer thickness up to 0.4 μm have been achieved. This process enables several-micron-thick PZT films being fabricated only by less than 10 steps of coating.

3. Crack-free and uniform PZT composite thick films have been deposited on platinized silicon substrate by using the novel powder-loaded sol-gel processing technology. PZT thick films with thickness ranging from several microns to 20 microns have been successfully fabricated onto silicon substrate.
4. In the development of a high-sensitivity interferometric method for piezoelectric characterization, a modulation technique has been proposed and realized to overcome the random drift problem of the fringes caused by the environment or even the intensity variation of the laser source. An ultrahigh out-of-plane displacement resolution down to pico meter required for piezoelectric characterization of thin films has been achieved.
5. Based on the modulation technique, a high-resolution scanning homodyne interferometer has been successfully developed for characterization of piezoelectric thin films as well as for vibration measurement of MEMS devices.
6. By employing the novel scanning characterization technique, some piezoelectric thin/thick film samples have been characterized with enhanced accuracy and consistency compared with single point measurements. The effects of several processing parameters, i.e., sol-gel concentration, powder-to-solution ratio, cold isostatic pressing, on the piezoelectric properties of the resultant PZT films have also been discussed.
7. A new processing for design and fabrication of piezoelectric pMUT for transmitter application has been successfully developed by combining the hybrid PZT film deposition technology with silicon micromachining. The fabricated prototype devices have been characterized in terms of membrane deflection, emitting sound pressure, and directivity of emitting ultrasound beam. High output *SPL* and desirable directivity patterns have been achieved.

1.4 Organization of the thesis

This thesis comprises of six chapters:

Chapter 1 gives a general introduction to the thesis.

Chapter 2 provides background knowledge on piezoelectricity and the related materials, followed by a brief introduction of the MEMS technology. The various techniques for deposition of lead zirconate titanate (PZT) thin/thick films on silicon substrate are introduced, with more emphasis placed on sol-gel method. The important issue of piezoelectric characterization for thin/thick films is then discussed in detail. Finally, applications of piezoelectric PZT thick films on silicon substrate for MEMS type devices are also discussed.

In Chapter 3, a hybrid sol-gel processing technology is developed for deposition of PZT thin/thick film on platinized silicon substrate. Phase analysis is carried out by X-ray diffractometry and infrared spectrometry. Microstructure of the films is examined using field emission scanning electron microscopy, and ferroelectric properties are characterized.

Chapter 4 devotes to the development of a modified scanning Mach-Zehnder interferometer and the scanning interferometric method for piezoelectric characterization of PZT films.

Chapter I Introduction

Chapter 5 focuses on the design and fabrication of diaphragm-type piezoelectric micromachined ultrasonic transducer (pMUT) arrays by combining the hybrid PZT thin/thick film deposition technology with bulk silicon micromachining technology.

Finally, the conclusion and recommendations are presented in Chapter 6.

CHAPTER TWO

BACKGROUND

In this chapter, background knowledge is firstly given on piezoelectricity and the related materials, followed by a brief introduction on the MEMS technology. The various techniques for deposition of lead zirconate titanate (PZT) thin/thick films on silicon substrate are then introduced one by one, with emphasis placed on the sol-gel method. The advantages and drawbacks of each technique are compared. The important issue of piezoelectric characterization for thin/thick films is then discussed in detail. Finally, applications of piezoelectric PZT thick films on silicon substrate for MEMS type devices are discussed. Three examples, micro-cantilever, micro-pump and ultrasonic array, are presented to show the significant importance of piezoelectric thin/thick films for MEMS applications.

2.1 Piezoelectric films for MEMS applications

2.1.1 Piezoelectricity and piezoelectric materials

The direct piezoelectric effect, discovered by Pierre and Jacques Curie in 1880, is described as the generation of a macroscopic polarization in certain dielectric materials when subjected to stress. Conversely, a strain can be caused in these materials by applying an external electric field. Even though piezoelectric phenomena had been known for many years, the real mechanisms were not well understood until a microscopic approach was carried out demonstrating that piezoelectricity was a bulk property rather than a surface effect, as it had been previously believed. In fact, the piezoelectric effect originates from internal structural variations in the materials. To understand the basic bulk mechanisms, we take PbTiO_3 (PT) piezoelectric ceramics as an example [1-3].

Figure 2.1 Crystal lattice structures of perovskite PT above T_c and below T_c .

Figure 2.1 shows the unit lattice cell of PbTiO_3 , which is a typical perovskite structure (ABO_3), featuring a corner-linked network of oxygen octahedra where Ti^{4+} ions occupy B sites in the octahedral cage and Pb^{2+} ions situate at A sites. Above the Curie temperature (T_c), the unit cell is a highly symmetric cubic phase without any net polarization. When the temperature is below T_c , the structure distorts into a lower symmetric tetragonal phase, accompanied by an off-center shift of smaller cation (Ti). As the centers of positive charge and negative charge are no longer at the same position, a dipole is resulted with a polarization oriented along the direction of Ti shift. All dipoles align in the same direction within a domain. Due to the randomly oriented domains, the material possesses no macroscopic piezoelectricity until an external electrical field is applied to align all the domains towards a certain orientation, which is the so-called poling process. When such a poled ceramic is subjected to stress, the macroscopic polarization will change due to the size variation of every dipole, causing a charge to build on the surfaces. Conversely, when the ceramic is subjected to an external electrical field, the size of dipoles and domains will also change, resulting in a macroscopic strain.

Piezoelectricity offers a direct electromechanical coupling effect, enabling it to be extensively used in many electromechanical devices for both sensor and actuator applications. The direct piezoelectric effect is currently being used to generate charge (voltage) in applications such as gas igniters, acoustic pressure sensors, vibration sensors, accelerometers, and hydrophones. The actuating applications, including piezoelectric motor, ink-jet heads for printers, noise damping system, precise positioners, acoustic and ultrasonic generators, make use of the converse effect. At high frequencies, piezoelectric transducers also function as frequency control devices, bulk and surface acoustic wave (SAW) resonators, filters, and delay lines.

Chapter II Background

Many single crystals and polycrystalline ceramics, such as quartz, ZnO, Rochelle salt, BaTiO_3 , $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ system, possess piezoelectricity. It has also been discovered that certain polymers, notably polyvinylidene difluoride (PVDF), show good piezoelectric properties when stretched during fabrication. Table 2.1 shows typical values of piezoelectric and mechanical properties of commonly used piezoelectric materials.

Table 2.1 Piezoelectric and other related properties of commonly used piezoelectric materials [3-5].

Materials	Relative Dielectric Const. (1kHz)	Piezoelectric Constant d_{33} (pC/N)	Electromechanical Coupling Coefficient k_{33}	Acoustic Impedance (MRayls)
Quartz	4.5	2.3 (d11)	0.1	/
ZnO	11	12.3	/	35.9
BaTiO_3	1700	191	0.21	/
$\text{Pb}(\text{Zr,Ti})\text{O}_3$	1300	289	0.7	36
PVDF	13	-33	0.19	4

These materials are employed for different applications according to their properties. Generally speaking, PZT has been extensively used for a wide range of applications due to its much better piezoelectric properties over the other materials. For a certain circumstance, however, many other factors should also be taken into account. Taking ultrasonic transducers for instance, two types of piezoelectric materials are generally used as transducer materials: lead zirconate titanate (PZT) and polyvinylidene fluoride (PVDF). PZT has high piezoelectric constant and electromechanical coupling coefficient, resulting in a high sensitivity. However, its

large acoustic impedance makes it very difficult to transmit ultrasonic energy into the air or human tissue, which has very low acoustic impedance. Therefore an additional layer for acoustic impedance match is inevitably required. On the other hand, PVDF has a very good acoustic impedance matching with human tissue, but its electromechanical coupling coefficient is rather low, resulting in low sensitivity. In addition, the low dielectric constant of PVDF also creates the problem of electric impedance mismatch, which limits the application of PVDF in array transducers.

2.1.2 Microelectromechanical system

Microelectromechanical systems (MEMS) integrate both electrical and mechanical elements that are built on such a small scale that they can be appreciated only with a microscope. MEMS elements interface with nonelectronic signals and often merge signal processing with sensing and/or actuating, thus providing a controllable conversion between electrical energy and mechanical energy.

Fully integrated MEMS are designed using computer-aided design (CAD) techniques based on very large scale integrated circuit (VLSI) and mechanical CAD systems; they are batch-fabricated using VLSI-based fabrication tools. The microelectronics technology was originally developed for implementation of integrated circuits (tiny pieces of semiconductor, usually silicon, fabricated to combine millions of transistors and other electronic devices to perform complicated tasks). The success of microelectronic manufacturing and the continuing trend toward miniaturization and cost reduction have led to universal use of this technology in the nonelectronic world and resulted in the adaptation of the VLSI tool-set to the

manufacture of systems that interface with the nonelectrical environment. Today the techniques of microelectronics are applied not only to produce electronic circuits, but also circuits that include optical, acoustical, magnetic devices and mechanical micro-machines, opening new opportunities for more advanced circuit capabilities. Research in this field began in the 1950s with breakthrough studies on piezoresistance in silicon. Single-crystal silicon's piezoresistance and elastic behavior made it an excellent material for the production of sensing devices and led in the 1960s to the development of the first silicon pressure sensors. In the 1970s, the field grew as pressure-sensor production increased and the first generation of silicon accelerometers were developed. The field of MEMS was boosted in the late 1980s after silicon fluid valves, electrical switches, and mechanical resonators were developed and marketed [6]. Like VLSI, MEMS are becoming progressively smaller, faster, and more functional.

2.1.2. Piezoelectric thin/thick films on silicon

The rapid development of MEMS has initiated a need of a number of piezoelectric materials to be integrated on silicon substrate for varieties of promising micro-devices, including micro-cantilever, micro-pump, micro-motor, ultrasonic array, etc. In these application cases, the minimized device size and process compatibility require on-chip integration of piezoelectric thin/thick films rather than bulk materials. Here the ‘thin’ and ‘thick’ are defined respectively as thickness ranges of ‘below several microns’ and ‘from several microns to hundreds of microns’. This definition is largely due to a technology gap of film fabrication. The ‘thin’ film fabrication can be realized by methods such as sputtering, pulse laser deposition, chemical vapor

deposition, sol-gel, whereas the ‘thick’ film fabrication usually employs the techniques such as screen-printing and tape casting.

2.2 Techniques for film preparation and integration

2.2.1 Sputtering deposition

A sputtering system consists of a stainless steel chamber connected with a high vacuum pumping system able to reduce the residual pressure below 10^{-6} mbar. Inside the chamber, a circular electrode on which is bonded the material to be sputtered (target) is placed in front of another electrode supporting on its surface the substrate to be coated. A proper voltage applied between these electrodes ionizes a gas introduced into the chamber and held at a suitable pressure. The ions of the gas bombard the targets, producing the ejection of target particles toward the substrate. If the gas is inert (i.e., Ar) the species deposited are the same as those of the target, while a proper mixture of inert and reacting gases determines the compound that will result as a combination of the reactive gas and the target species [7].

This rather mature technique is widely used for the thin film deposition of piezoelectric materials like ZnO, AlN, at a relatively low processing temperature. The resultant films have strong adhesion to the substrate, uniform properties and thickness over large areas. However, due to the difficulty of stoichiometry control, sputtering is not suitable for deposition of multicomponent materials such as PZT, which is highly compositional sensitive, i.e., small variations in the film stoichiometry result in a strong degradation of piezoelectric and ferroelectric properties. Even though, some

research did manage to carry out magnetron sputtering of a multielement (Pb, Zr, Ti) metal target with sector areas optimized to obtain the desired film composition [8].

2.2.2 Pulsed laser deposition

Pulsed laser deposition (PLD) is an emerging technique for thin film deposition. It is based on material removal by bombarding the surface of a target with short energetic pulses of a focused laser beam (laser ablation). This process takes place in a vacuum chamber where a gas is held at constant pressure. Due to the high power density of the beam, a plume shaped plasma perpendicular to the target surface is generated at the incident point. The plasma contains ions of target and of the gas atmosphere. Condensation of the particles ejected from the target produces the growth of a thin film on the substrate, which is placed few centimeters apart from the target. The film composition can be the same as the target, if the atmosphere is inert, or a compound of target species and reactive gas. During the deposition process the target must be continuously rotated and translated to avoid crater formation and to obtain uniform erosion [7].

PLD possesses some particular advantages, including the direct transfer of complicated stoichiometries from bulk material into a thin film, no charge effect, low deposition temperature, and sometimes, no subsequent thermal treatments required. The main drawback of this technique comes from the formation of particulates (droplets) on the substrate and film surface.

2.2.3 Chemical vapor deposition (CVD)

This synthesis method is based on the reaction of the constituents in the vapor phase and the formation of the solid film on the substrate surface. CVD offers large-scale deposition, step coverage, easy control of composition. However, this technique normally requires high processing temperature, and includes many corrosive chemical compounds, which may be highly toxic [7].

2.2.4 Sol-gel method

Sol-gel is one of the widely used methods for the deposition of different materials in thin film form, due to its advantages over other techniques, such as control of composition over a large area, low initial processing temperature, high purity, and low cost. A typical sol-gel deposition process usually involves: (1) mixing of liquid material components (metal alkoxides) in adequate proportion to obtain sol; (2) transformation of sol into gel precursor by hydrolysis reaction; (3) preparation of a homogeneous solution containing the precursor; (4) deposition of the solution on the substrate by spin-coating or dip-coating to produce a wet thin film; (5) drying and thermal processing whereby the organic components are removed and crystallization achieved. Usually the single-layer thickness is below 0.3 μm . Multiple coating is required to reach the desired thickness.

Ease of stoichiometric control and low cost make sol-gel method a competitive technique for thin film fabrication of multi-element materials such as PZT. Extensive research on the choice of starting chemicals, solvents, as well as the handling conditions and firing procedures have been carried out on the thin/thick film

deposition of PZT using the sol-gel technology [9-12]. However, the technique encounters difficulty in thick film fabrication due to the single-layer thickness limit, around 300 nm, above which cracking usually occurs. Therefore, multiple coating of up to hundred times has to be carried out to achieve a thickness of several tens of microns. This process is time-consuming and impractical from industry point of view. To overcome this difficulty, Barrow et al. developed a sol-gel based ceramic-ceramic 0-3 composite coating technique by dispersing ceramic powders into the sol-gel solution to obtain a much larger single-layer thickness (several microns) as well as to avoid cracking [13]. The composite solution can be spin-, dip- or spray- coated onto substrate, fired and annealed in a manner similar to that of sol-gel technique. By multiple coating, thick films with thickness of several tens of micrometers have been successfully deposited onto various substrates [14].

With respect to sol-gel film deposition, the following issues are worth taking note of:

(a) Route selection

Most of the reported sol-gel works for thin film preparation are based on a methoxyethanol route to make sol solutions of lead acetate and Ti, Zr alkoxide [9]. This route is suitable for fabricating single-layer PZT films no thicker than 0.1 μm . Beyond this thickness limit, cracking problem arises. Therefore, multiple coating of more than 30 layers is required to fabricate films of several microns thick. This is time-consuming and impracticable in industries. Modifications have been made by adopting several other routes, such as acetic acid, 1,3-propanediol and triol. Milne and co-worker reported a 'diol sol-gel route' that allowed single-layer PZT films as thick as 1 μm to be formed crack-free [15]. However, the high viscosity of the sol makes it

increasingly difficult to eliminate organic decomposition products without physical disruption of the film structure. Having a viscosity between those of MOE and diol, acetic acid seems to be a promising route for fabricating thick, dense, crack-free films. Recently, this type of sol has been used to build up multi-layer films in the thickness range 1-12 μm , with a single layer thickness of 0.3 μm [16]. Other than the viscosity factor, the various solutions have shown different effects on the crystallization process of PZT. The mechanisms remain vague at present. Further comparison of different routes is needed to evaluate the solvent factor on the film properties.

(b) Phase evolution

Generally, it is assumed that the phase transformation steps are as follows: from amorphous phase to pyrochlore phase, and, finally, to perovskite phase. It was demonstrated by intermediary analysis that the activation energies of the phase transformation for the two processes are similar, i.e., the pyrochlore phase, which is detrimental to the piezoelectric property of resultant film, competes with the ferroelectric perovskite phase during thermal processing [10]. Issue thus arises on how to minimize the pyrochlore proportion in the resultant film for a better piezoelectric performance. The phase evolution is dependent on the reaction route, annealing treatment, and substrate structure. Different mechanisms concerning the direct perovskite phase growth have been proposed, such as the lattice match between Pt (111) and PZT (111), the promoting of PZT nucleation by Ti diffusion through the Pt layer at the Pt-Ti interface and the formation of a Ti-enriched phase that favors the perovskite growth, the formation of an intermediate layer, with the composition Pt_xPb , etc. [11]. These assumptions need to be confirmed.

In addition, as the crystallization process of different phases is highly sensitive to heat treatment procedure, it is necessary, therefore, to thoroughly investigate the crystallization kinetics of the phase transition process. On this basis, a further optimization of heat treatment parameters such as temperature, heating rate, holding time, can thus be made.

(c) Substrate and buffer layer

Various types of substrates have been employed for PZT film coating. Silicon, sapphire and glass are the most frequently used ones. Y.L. Tu and coworker reported successful deposition of crack-free PZT thick films up to 10 μm onto platinized sapphire substrate [12]. K. Yokosawa et al. fabricated a high frequency ultrasonic transducer with sapphire serving both as the substrate and as the acoustic focusing lens [17]. However, silicon still remains the most important one among all the substrate candidates. This is for good reasons: (a) the excellent mechanical properties of single crystalline silicon; (b) the well-established micro-machining technologies for silicon; and (c) the possibility of integrating MEMS devices together with the control circuits for further miniaturization of the entire system and higher operating frequency. Due to a larger difference in thermal expansivity with PZT, however, it is more difficult to deposit crack-free PZT films on silicon than on sapphire. Therefore, how to deposit thick, crack-free PZT films on Si substrate remains to be a technical challenge.

Buffer layer is the intermediate layer between the substrate and the bottom electrode. It plays an important role on facilitating perovskite nucleation as well as on preventing peeling off of bottom electrode from substrate during high-temperature annealing.

(d) Cracking

Due to the thermal expansion difference of PZT film and Si substrate, and the removal of organics during processing, the resultant films always bear a tensile stress and are easily cracked. Taking ‘methoxyethanal (MOE) sol-gel route’ for instance, the single-layer thickness limit is 0.1 μm , beyond which cracking occurs. Many attempts have been made on increasing the thickness of single layer without cracks. Some other workers incorporated polyvinylpyrrolidone (PVP) in coating solutions and increased the single layer thickness to $> 1 \mu\text{m}$ [18]. But the resultant films were rather porous because of a large amount of organics being removed. It was also found that the crack formation is sensitive to thermal processing procedure [19]. But the detailed mechanisms are still not clear.

2.2.5 Screen printing and tape casting

Screen printing is a technique that an image is transferred to the printed surface with ink, which is pressed through a stenciled screen and treated with a light-sensitive emulsion. Film positives are put in contact with the screens and exposed to light, hardening the emulsion not covered by film and leaving a soft area on the screen for the squeegee to press ink through (also called silk screening). Another technique is pad printing: a recessed surface is covered with ink. The plate is wiped clean, leaving ink in the recessed areas. A silicone pad is then pressed against the plate, pulling the ink out of the recesses, and pressing it directly onto the product.

Tape casting also is known as doctor blade or knife coating. The process utilizes a scraping blade for the removal of excess substances from a moving surface being coated. Since its inception, tape casting has been used to produce thin layers of ceramic-loaded polymers that can be used as single layers or can be stacked and laminated into multilayered structures [20].

Recently, both techniques have been employed for thick film deposition of PZT [21]. The thickness achieved can be as large as several hundreds microns. However, the resultant films have a porous structure, and the high sintering temperature makes the techniques incompatible with conventional silicon IC process.

2.3 Piezoelectric characterization for thin/thick films

The application of piezoelectric thin/thick films on silicon substrate for various MEMS devices requires intensive investigation of piezoelectric properties in thin films. With the thickness shrinking to the magnitude of microns, the piezoelectric performance of the thin film material is increasingly dependent on various factors such as the lattice orientation, cavity or defect density, substrate constraint and film thickness itself. The effective piezoelectric properties for thin films may exhibit a difference from those of bulk materials. Much work has been done on the piezoelectric coefficient measurement of thin films and a number of innovative techniques have been established. However, discrepancy among the reported data in the literature is significantly large [22-25], suggesting many of the measurement techniques might not be accurate or reliable. There is an urgent need to develop a widely accepted standard method for piezoelectric characterization of thin films.

2.3.1 Direct methods

This category of method makes direct use of the piezoelectricity, which can be either the direct effect or the converse effect, of the material to be tested. For sensing applications, the direct-effect-based methods, e.g., normal load method, are employed to measure the charge produced by applying a certain stress in the sample. Hydraulic or pneumatic loading techniques have been developed [26, 27], in an effort to avoid damaging the delicate MEMS structure. For actuating applications, the piezo-induced displacements are to be detected. The order of magnitude of the displacement being measured for piezoelectric thin films usually ranges from sub-angstrom to several nanometers. Sensitive system such as interferometers and AFM should be employed in this case.

AFM has been recently modified for this purpose and shows some advantages [28]. It allows 2-D scanning of the sample surface. The sample surface is also not necessarily smooth. However, the inability to single out the film deformation from substrate motion limits its use for applications such as micro-cantilevers. Attempt has been made to minimize the effect of the applied electric field on the microscope tip. The results on various piezoelectric materials have been reported [28].

Various sorts of interferometers, notably the Michelson or Mach-Zehnder interferometers, provide more reliable means for displacement measurement. J.F. Li et al reported a simple but precise single-beam Michelson interferometry system for piezoelectric characterization [29]. An ultra-high resolution up to 10^{-4} Å was achieved. For d_{33} measurement of piezoelectric thin films, however, it is shown that vibrational

response measured with a single-beam interferometer includes a large contribution from the bending motion of substrate. To suppress this unwanted contribution, a variety of methods have been proposed [30]. W.Y. Pan and L.E. Cross introduced a double-beam system to examine the front face as well as the back face of the sample [31]. The effect of substrate bending was effectively eliminated.

With regard to the double-beam interferometric system, several aspects should be taken into account. Firstly, this method assumes that the front surface and the back surface of the substrate deform the same amount at the point of investigation. The assumption is only valid when there is no substantial localized deformation of the substrate just below the top electrode. Secondly, the front probing beam and the back probing beam must be strictly aligned to the same line. A deviation of only 0.2 mm of the two beams would bury the thickness dilatation of the film into the substrate bending motions and nullify the measurement results. Also, the double-beam interferometric method requires the samples to be double-side polished. Otherwise, it is difficult to achieve desired resolution or sometimes even difficult to obtain interference fringes, due to the light scattering at the unpolished surfaces and intensity loss on the increased optical components and lengthened optical path for the double-beam interferometer. Any of the above mentioned aspects, if not being carefully investigated, would limit the practical application of the double-beam system.

A novel method using a commercially available laser scanning vibrometer (LSV) has been reported [32] by K. Yao et al. This method measured the 2-dimensional vibration modality of a piezoelectric thin film as well as that of the surrounding substrate. The longitudinal dilatation is obtained by numerical summation of the

displacement of the film and that of the substrate. This method possesses several unique advantages over the single-point displacement detection methods, including high reliability, high efficiency, offering comprehensive information, easy sample mounting and fast optical alignment. Furthermore, the data obtained by this scanning technique yield much more information than that obtained by the single-point measurement using a double-beam system. For example, the substrate deformation can be easily and accurately measured by a line scanning, which is closely related to the transverse piezoelectric coefficient (d_{31}) of the films as well as the mechanical properties of both the piezoelectric film and the substrate. Given a proper analytical model or finite element model, it is possible to use the deformation data to work out the transverse piezoelectric coefficient or other mechanical properties of the piezoelectric films.

2.3.2 Indirect methods

Indirect methods are based on the piezoelectric induced effect, e.g., the bulk or surface acoustic wave response. These techniques, usually referred to as dynamic methods, rely more or less on the frequency resonance effects observed for a geometry-specified sample consisting of piezoelectric films sandwiched with top electrode and bottom-electrode-coated substrate. The piezoelectric properties of the thin films, d_{33} or e_{33} , are calculated on the basis of material properties as well as the geometry data of the structure. From the computational reliability point of view, indirect methods are complicated by the uncertainty over the material properties of the thin films.

Meitzler and Sittig gave a detailed description of bulk acoustic wave scheme for evaluation of d_{33} for a piezoelectric thin film transducer [33]. Cheeke et al. presented another example of d_{33} evaluation for PZT thin films from impedance spectrum of a two-layer resonator [34].

2.4 Piezoelectric MEMS devices

Microelectromechanical systems (MEMS) are currently viewed as providing enormous opportunities for perceiving and controlling a variety of physical environments. Numerous MEMS devices forming sensors, actuators, and micro-optical components have been demonstrated based on a wide variety of physical operating principles. To provide the electromechanical coupling, various mechanisms, such as electrostatic, electromagnetic, electrothermal mechanisms, have been proposed and demonstrated for MEMS applications [35, 36]. Each mechanism has its advantages and drawbacks, and is suitable for different circumstances. Usually those non-piezo mechanisms can generate a large displacement but suffer from a low speed of dynamic response, low force and a rather complicated structure, whereas the piezoelectricity, an intrinsic property of the material, provides the most direct electromechanical coupling with much faster dynamic response and larger force. With the rapid technological development aiming at further miniaturization of device size and higher operating frequency, faster dynamic response are becoming increasingly preferable. The piezo-MEMS thus offer a more promising and applicable solution for these application requirements. Furthermore, compared with electrostatic MEMS, piezoelectric MEMS usually possess much simpler structures. From the viewpoint of

reliability, simpler structures are preferred because they are generally less subject to failure problem.

Piezoelectric MEMS are usually operated in one of the two modes: sensing or actuation. When used as an actuator, a voltage is applied across a set of electrodes thereby inducing a strain or deformation in the film. This controlled deformation is used to do actuation. 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.

Several typical application examples of piezoelectric MEMS are presented below:

(a) Micro-cantilever

Micro-cantilevers possess a simple structure, but are widely applicable to a number of important applications, such as flow sensor, accelerometer, precise positioning, and other micro-actuators [37, 38]. Figure 2.2 shows an example of PZT driven micro-cutter for medical surgery [39]. The PZT layer is sandwiched between top and bottom electrode. When alternating voltage is applied, a vibrational motion is generated in the cantilever, driving the silicon blade to perform cutting of tiny tissues in human body.

a. Micro-cutter for medical surgery

b. Micropump for drug delivery systems

Figure 2.2 Two examples of piezoelectric MEMS devices.

(b) Micro-pump

Fully integrated drug delivery systems exploit on-chip micropumps for fluid handling [40]. A variety of chemical and biological procedures require devices that can deliver minute and accurately metered quantities of material. Diabetics, who are afflicted to such a degree that they have to be administered a certain dose of insulin at a constant rate, need a small pump that can be used to inject small amounts of this drug. For other treatments, such as chemotherapy for cancer patients or for pain relief of terminally ill patients, a small pump that can administer small amounts of drugs at a well described and preferably programmable rate is a very necessary part of the therapy.

Piezoelectric micropumps, driven by the vibrational motion of a piezoelectric actuator, can be classified into two groups: pumps with check valves and valveless pumps. Many micropump designs are based on a single actuator combined with one-way valves to limit the flow to a single direction [41, 42]. One-way valves are difficult to fabricate and may break or foul in operation. To overcome these difficulties, valveless fluidic diodes were developed with converging/diverging nozzles to produce a preferential flow direction (see Figure 2b). These are simple to fabricate and resist to fouling [43], but the diodic structures may take up significant area on the chip surface.

All the micropumps mentioned above share the limitation of being inherently unidirectional. Another group of valveless micropumps, being driven with a finite number of fixed actuators, is based on peristaltic mechanisms [44, 45]. Flow is induced by proper phasing of the actuation sequence, approximating a traveling wave. Peristaltic micropumps allow bi-directional flowing, but suffer from a much more complicated control circuits.

(c) Ultrasonic transducer and phased array

Ultrasonic imaging and detecting possess several unique advantages over other techniques. The image presentation is in real time, which permits the identification and study of moving internal structures. Its non-destructive nature enables the technique to be used for in vivo imaging of tissues, and aids much of its clinical acceptance [46].

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a. Diaphragm structure of single transducer element;

b. Ring arrays with different patterns showing the directivity of ultrasound reception.

Figure 2.3 Ultrasonic array using PZT thin film technology [47].

In an ultrasonic imaging system, ultrasonic transducers perform the transmission and reception of ultrasound signal. When it is working in a pulse-echo mode, the single transducer serves both as sensor and actuator. Many single transducers can be integrated on one substrate with certain inter-spacing to form a transducer array. This array of transducers is properly phased to achieve high directivity as well as precise focusing of the ultrasound beam. Ultrasound wavelength determines directivity pattern of the array when the elements are arranged regularly at equal spacing.

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Sharpness of the directivity is almost in proportion to the ratio of the size of array to the wavelength [48], and large spacing between adjacent elements makes large side lobes when the wavelength is fixed [49].

Figure 2.3 presents an example of ultrasonic sensing array based on sol-gel thin film deposition of PZT [47]. The single element has a diaphragm structure, with a working frequency of 176 kHz. The elements are arranged in a manner of the ring array, which is believed to be more efficient in sense of directivity than a matrix array with the same number of elements [50].

CHAPER THREE

DEPOSITION OF PZT FILMS ON SILICON USING HYBRID PROCESSING TECHNOLOGY

3.1 Introduction

In this chapter, a hybrid sol-gel processing technology is developed for deposition of PZT thin/thick film on platinized silicon substrate. The chapter includes three parts: The first one is a study of sol-gel routes. The crystallization kinetics is investigated by thermal analysis method: PZT gels are prepared using three different routes; thermal analyses (DTA and TGA) are performed for the gel samples; and several kinetic parameters of phase formation during firing are calculated using Kissinger's method. The aim of this study is to provide detailed information about the phase formation

process. Based on such information, an optimization of sol-gel processing can be made for the PZT film fabrication. The second and third parts devote to a modified ‘acetic acid sol-gel route’ for PZT thin film deposition on silicon and a hybrid technology for PZT thick film deposition, respectively. Phase analysis is carried out by X-ray diffractometry and infrared spectrometry. Microstructure of the films is examined using field emission scanning electron microscopy, and ferroelectric properties are characterized.

3.2 Study of sol-gel routes

3.2.1 Sol-gel preparation

The starting reagents used for PZT precursor are lead acetate trihydrate (Riedel-de Haen), zirconium acetylacetonate (Fluka Scientific), titanium isopropoxide (Sigma-Aldrich), and acetylacetone (Fluka Scientific). The mole ratio of Zr to Ti is made 53:47 of the morphotropic phase boundary, where an optimized piezoelectric property can be achieved.

Due to the moisture-sensitive nature of Ti-alkoxide, the titanium isopropoxide is firstly chelated with acetylacetone in mole ratio 1:1 by heating and stirring the mixture at 80°C for 10 minutes. During this process, one isopropoxide group of Ti-alkoxide is replaced by acetylacetone, which reduces the hydrolysis rate of Ti-alkoxide and makes it stable in open air for a long period of time.

The second step is to obtain a Ti-Pb mixture by dissolving lead acetate trihydrate into the stabilized titanium isopropoxide at 160°C with continuous stirring for 10

minutes. 10mol% excess lead acetate trihydrate is added to compensate the lead loss during the later heat treatment.

After dissolving zirconium acetylacetonate into the Ti-Pb compounds at 210°C with continuous stirring for 30 minutes, light yellow sticky solution is obtained. The solution is then baked in a vacuum furnace at 80°C for 4 hrs. In this way, most of the volatile organics are removed and light yellow xerogel powder is resulted.

Three kinds of 40% (wt%) sol solutions are prepared by dissolving the precursors into acetic acid, 2-methoxyethanol, and 1,3-propanediol, respectively. Further removal of solvents is performed by baking the as-prepared solutions at 80 °C for 6 hrs in order to minimize the burning effect of organics, which might cause problem to the DTA analysis. Afterward, brown glass-like solidified gels are obtained. The condensed solids are ground to powder for further analyses.

3.2.2 Thermal analyses

The three types of samples are analyzed with a Perkin-Elmer DTA-7 scanning from 30 °C to 750 °C at heating rates of 2 °C/min, 3.5 °C/min, 5 °C/min, 6.5 °C/min, and 8 °C/min, respectively. The exothermal peak shifts at different heating rates are thus evaluated. At the same time, a Perkin-Elmer TGA-7 is also employed to measure the weight loss of samples as a function of temperature during heating.

3.2.3 General descriptions of DTA/TGA curves

Figure 3.1 DTA/TGA curves (5°C /min) of the samples using acetic acid as solvents.

Figure 3.2 DTA/TGA curves (2°C /min) of the samples using MOE as solvents.

Figures 3.1 and 3.2 show typical DTA curves superimposed with the corresponding TGA curves of the samples using acetic acid and MOE as solvent. It is evident that three steps make up the whole heating process. The first step is from 200°C to about 300°C, featuring several closely gathered exothermal peaks and 20% weight loss of the samples. This step is dominated by the combustion reactions of organics, suggesting a pre-firing step at no less than 300°C be involved in the thin film processing for organic removal. The next step between 350°C to 400°C is characterized by a short blunt exothermal peak in the DTA curve and a flat TGA curve, which implies that a secondary phase transition without any weight loss takes place in the temperature range. Some work of XRD analysis [51, 52] has identified that the formation of an intermediate pyrochlore phase ($A_2B_2O_7$) takes place in the sol-gel derived PZT when heated above 350°C. Therefore, it is reasonable to associate the short blunt exothermal peak with the crystallization process of pyrochlore phase.

During the third step from 400°C to 520°C, two exothermal peaks, a tall sharp one on the left and a lower blunt one on the right, emerge in the DTA curve. The two peaks have such a close distance that the shorter one is almost indistinguishable. In addition, the corresponding part of TGA curve shows that the weight of the sample starts to decrease again from 400°C, the onset of the sharp exothermal peak. The process ends up at around 500°C with 2.5-5% of weight loss. According to some reported XRD analyses results [51], this step should be related to the process of pyrochlore-perovskite phase transition. This phase transition shall include two steps, a former step of pyrochlore de-oxygen process ($A_2B_2O_7 \rightarrow 2ABO_3 + O$), which theoretically accounts for 2.4% weight loss for PZT(53/47) system, and a latter one of perovskite crystallization at about 500°C. After 530°C, the sample experiences no more phase changes, leaving a flat DTA curve and a flat TGA curve as well till the

end of temperature scanning. For the de-oxygen process, the measured weight loss from TGA curve of acetic acid routed sample agrees well with the theoretical value, where as the weight loss of MOE routed sample is higher, suggesting that residual organic ligands do exist at higher temperature and the organic removal is still going on during the phase transition.

Figure 3.3 DTA/TGA curves (2 °C/min) of the sample using 1,3-propanediol as solvent.

The DTA/TGA curves for the sample using 1,3-propanediol as solvent in Figure 3.3 shows much discrepancy against the curves for the samples prepared by the other two routes. The sharp peak in the third step is more than one order of magnitude higher and corresponding to a much more weight loss (7.5%) than those in previous two cases. Obviously, besides the de-oxygen process, some kind of combustion reactions of residual organics must have taken place, which result in the abrupt temperature increase and considerable weight reduction. This result indicates that higher temperature is required to totally decompose diol ligands. The existence of

residual organic ligands at high temperature may cause the inhomogeneous distribution of Pb, Ti, and Zr components of the material [52]. As pyrochlore phase is favored in Pb-deficient area [53], the perovskite structure cannot be fully formed unless the residual organic ligands are completely removed. However, the high exothermal event may also have some positive effect on the process of phase transition. More studies are needed to further evaluate the effect of this reaction on the phase transition process.

3.2.4 Calculation of activation energies

Thermal analysis instruments can be used to investigate the reaction rate kinetics of a broad range of materials [54]. The two basic approaches to determine reaction rate kinetic parameters are isothermal methods and non-isothermal (dynamic) methods. In an isothermal experiment the sample is quickly brought to a predetermined temperature where the thermal analysis instrument monitors the behaviour of the system as a function of time. Non-isothermal methods record the response of the sample as it is scanned, usually at a constant rate although hyperbolic temperature programmes are sometimes used.

Reacting systems are divided into two classes, homogeneous and heterogeneous. In homogeneous systems the rate of reaction is determined by measuring isothermally the decrease in concentration of the reactant or the increase in concentration of the product. However, almost all solid-state reacting systems are heterogeneous in nature. The heterogeneity can be compositional and/or structural. In this case, thermal analysis is generally carried out using non-isothermal methods.

The expression for the rate of reaction of a heterogeneous system has the following general form:

$$\frac{d\alpha}{dt} = -kf(\alpha)h(\alpha, T) \quad (3.1)$$

where the function $h(\alpha, T)$ is normally taken to be equal to unity, α is the concentration of reactant defined as:

$$\alpha = \frac{m_s - m}{m_s - m_f}$$

where m_s , m and m_f are initial, actual and final mass of the sample, respectively, and k the rate coefficient, which is given by the Arrhenius equation:

$$k = A \exp\left(\frac{-E}{RT}\right) \quad (3.2)$$

The unit of k is s^{-1} ; $A(s^{-1})$ is sometimes called the frequency factor, E (kJ/mol) is the activation energy, T (K) is the temperature of the sample and R (J/molK), the gas constant.

The functional form of $f(\alpha)$ is dependent on reaction mechanisms. It is commonly presumed that, for solid-state reactions $f(\alpha) = (1 - \alpha)^n$, where n is the reaction order and is assumed to remain constant for the duration of the reaction.

Under dynamic conditions the sample temperature is presumed to be a function of time only and equal to the furnace temperature, therefore, $dt = \nu(T)dT$. Substituting it into equation (3.1) we obtain:

$$\frac{d\alpha(T)}{dT} = -A \exp\left(\frac{-E}{RT}\right) \nu(T) f[\alpha(T)] \quad (3.3)$$

For a linear heating programme with constant heating rate, ϕ , $dt = \phi^{-1} dT$, and equation (3.3) becomes:

$$\frac{d\alpha(T)}{dT} = -\frac{A}{\phi} \exp\left(\frac{-E}{RT}\right) f[\alpha(T)] \quad (3.4)$$

On the basis of the above equations, Kissinger's method is proposed, originally for calculating kinetic parameters for reactions of the type solid $\rightarrow$ solid + gas from DTA experiments. An important assumption of this method is that the maximum in the DTA curve occurs at the same temperature as the maximum reaction rate, which means $\frac{d^2\alpha}{dt^2} = \frac{d^2\alpha}{dT^2} = 0$ (for constant heating rate program only), when T reaches T_M , i.e., the peak maximum temperature. From equation (3.4) it follows that:

$$\frac{E\phi}{RT_M^2} = A \exp\left(\frac{-E}{RT_M}\right) \left. \frac{df(\alpha)}{d\alpha} \right|_{T=T_M} \quad (3.5)$$

For most of the reaction mechanisms, the rightmost factor of equation (3.5) is insensitive to both ϕ and T_M , therefore, by taking natural logarithms, we obtain:

$$\ln(\phi/T_M^2) \propto \frac{E}{R} \cdot \frac{1}{T_M} \quad (3.6)$$

Equation (3.6) provides a means of calculating the activation energy from DTA results. When $\ln(\phi/T_M^2)$ is plotted against $1/T_M$, E can be calculated from the slope of the best-fit line. A generalized form of the Kissinger's method has also been applied

[55] to study the crystallization behavior of BST as well as to determine some important parameters in the kinetic equations that described the process of crystallization.

DTA curves at different heating rates (2, 3.5, 5, 6.5, 8 °C /min) are superimposed into one diagram to demonstrate the dependence of peak position on heating rate as given in Figures 3.4 and 3.5. There is an evident trend that the peaks shift rightward as heating rate increases.

Figure 3.4 DTA curves at different heating rates for the sample using acetic acid as solvent.

Figure 3.5 DTA curves at different heating rates for the sample using MOE as solvent.

Figure 3.6 An example of Gaussian multi-peak fit for a DTA curve (MOE, 8 °C /min).

To quantify the peak positions, a simple way is to find several maximum ΔT_s and the corresponding temperatures (T_M). Due to the severe overlapping of different peaks, however, it would be inaccurate to determine the peak temperatures this way, or even impossible to find peaks when some low peaks are almost covered by higher ones very close to them. For example, the perovskite crystallization peak is hardly detectable because of its strong interference with the higher de-oxygen peak. To overcome this difficulty, a Gaussian multi-peak fit technique is employed and desirable results are obtained as shown in Figure 3.6. The T_M s of three peaks of interest, pyrochlore crystallization, de-oxygen, and perovskite crystallization peak, are determined by this method and $\ln(\phi/T_M^2)$ versus $1/T_M$ are plotted for each peak as shown in Figures 3.7 and 3.8. The data reveal good linear relations.

Figure 3.7 Linear fit of $\ln(\phi/T_M^2)$ versus $1/T_M$ data (de-oxygen reaction of MOE gel).

Figure 3.8 Linear fit of $\ln(\phi/T_M^2)$ versus $1/T_M$ data (de-oxygen reaction of HAc gel).

The activation energies of different peaks are calculated from the slopes of the plots and the results are listed in Table 1.

Table 3.1 Calculated activation energies for several reactions.

Solvent	E (kJ/mol) for pyrochlore crystallization	E (kJ/mol) for de-oxygen process	E (kJ/mol) for perovskite crystallization
Acetic acid	52.6	246.7	74.2
2-methoxyethanol	/	457.2	68.1

It should be noted that the second step of the DTA curve of MOE route sample is different from that of acetic acid route one. It can be seen from Figures 3.4 or 3.5 that, as the heating rate increases, a combustion peak is moving from the first step into the second one, and the lower peak of pyrochlore crystallization is totally covered. This is

verified by the corresponding TGA curves in which the flat stage of pyrochlore crystallization is replaced by a down slope, indicating some decomposition of organics are going on. The combustion peak makes it impossible to determine the position of pyrochlore peak, nor to calculate the activation energy.

No attempt has been made to determine the crystallization peak temperatures for propanediol-routed sample, as the very high exothermic peak obscures the other low peaks adjacent to it, and makes it impossible to accurately determine the positions of other peaks.

The data listed in Table 1 clearly show that the activation energy for pyrochlore crystallization is much lower than that for pyrochlore de-oxygen process, which is a necessary step to perovskite structure. This result suggests that the process of pyrochlore crystallization is much easier and faster to occur than that of the de-oxygen process. Table 1 also shows that the activation energy for de-oxygen of MOE gel is almost two times of that for acetic acid gel, which means the phase transition of acetic acid gel should be much easier than that of MOE gel. This can be taken as an advantage of acetic acid over MOE as solvent.

3.3 PZT thin film deposition using acetic acid sol-gel route

Dense PZT (53/47) thin films are deposited onto silicon substrate using a modified ‘acetic acid sol-gel route’. Phase analysis is carried out by X-ray diffractometry and infrared spectrometry. Microstructure of the films is examined

using field emission scanning electron microscopy, and ferroelectric properties are characterized.

3.3.1 Experimental Procedure

3.3.1.1 Preparation of acetic acid based sol solutions

The starting reagents used for PZT precursor are lead acetate trihydrate (Riedel-de Haen), zirconium acetylacetonate (Fluka Scientific), titanium isopropoxide (Sigma-Aldrich), and acetylacetone (Fluka Scientific). The mole ratio of Zr to Ti is made 53:47 at the morphotropic phase boundary, where an optimized piezoelectric property can be expected. The details of preparation of xerogel precursor are described in Section 3.2.1.

In this experiment acetic acid is chosen as a solvent. Generally the PZT precursor is easily dissolved in acetic acid, provided the concentration is below 20%wt, a concentration too low to achieve a single layer film with thickness more than 200nm. In order to reduce the repeating times of multiple coating, more concentrated sol should be employed. However, the acetic acid based PZT sol become very unstable, sensitive to ambient temperature and concentration itself, when the weight ratio exceeds 22%wt, and the final resultant sol is always a suspension rather than colloid. It is found that, at high concentration (>40%wt), an extra amount of water facilitate the formation of stable sol. The detailed procedure of sol preparation is as follows.

Firstly the precursor and acetic acid are mixed at a weight ratio of 1:1, heated at 80°C with stirring for 20 minutes. After this step, 50%wt suspension is results.

De-ionized water is then added drop by drop into the suspension with continuous stirring until the mixture become clear. Acetic acid based sol with a concentration around 50%wt is thus obtained.

The concentrated sol can be further diluted with acetic acid into different concentrations (25%wt ~ 50%wt), corresponding to single layer thickness ranging from 150 nm to 500 nm.

By this method, clear brown solution with a concentration of 35%wt is prepared for film fabrication. Owing to the chelating step in precursor preparation, hydrolysis of Ti alkoxide is prevented, whereby the addition of water does no harm to the stability of the sol. The obtained sol has been stable for months, with no precipitation, suspension or gelation observed.

3.3.1.2 Deposition and thermal processing

Films are deposited by spin coating at 3000 rpm for 30 second onto two kinds of silicon substrates, Pt/Ti/SiO₂/Si and Pt/TiW/SiO₂/Si.

The as-coated films are firstly placed onto a hotplate for 1 minute to remove organics. According to the DTA study of acetic acid routed PZT gel in section 3.2, the pre-baking temperature is set to 350°C. The samples are then transferred immediately to a furnace at 550°C or 600°C for another 1 minute. This turns out to be a key step to prevent the initiation and extension of macrocracks in the films. Multiple coating is performed by repeating the above steps for several times until required thickness is reached. Final firing of multi-coated samples is conducted in a furnace at 650°C for 30 minutes. The overall procedure for sol preparation and film fabrication is shown in Figure 3.9.

Figure 3.9 Flow charts for sol preparation and film fabrication.

Crack formation is examined during the film fabrication process. Initial experiments included only one pre-baking step at 400°C between each coating. However, macroscopic cracking (obvious to naked eyes) is inevitable when total thickness of the film reached 800 nm. This problem is dramatically reduced by introducing a pre-annealing step at no less than 550°C for 1 minute, enabling a thickness of more than 2 μm to be reached without obvious cracks. Even so, the single layer thickness can be no more than 500 nm, a critical thickness beyond which cracking occurs immediately while the sample being placed into furnace for pre-annealing.

3.3.2 Phase Identification

Phase analysis is carried out on a Siemens 5005 X-ray diffractometer for samples experiencing different processing steps. Infrared reflection spectra are also measured using a Fourier-transform infrared spectrometer (Perkin-Elmer 2000). Film thickness and microstructure are studied by field emission scanning electron microscopy.

Figure 3.10 presents the XRD patterns of samples at different processing steps. The pattern of the film baked only at 350°C hotplate shows no distinct peaks, indicating an amorphous microstructure. After pre-annealing at 550°C, the sample exhibits pyrochlore phase ($A_2B_2O_7$) in its XRD pattern, featuring peaks at 29.4° (110), 33.6° (111), 49.2° (200) and 58.5° (220). By raising the pre-annealing temperature from 550°C to 600°C, a mixed pattern of pyrochlore phase and perovskite phase is observed. After final annealing at 650°C for 30 minutes, almost all the pyrochlore phase transformed to perovskite phase, as revealed in the clear perovskite-type pattern characterized by peaks at 21.9° (100), 31.0° (110), 38.2° (111) and 44.6° (200).

The infrared reflection spectra of samples at each processing steps are shown in Figure 3.11. The curve of the sample baked only at 350°C shows one peak at 1550 cm^{-1} , which can be attributed to the stretching vibration of C-O bond in CH_3COO -ligand. This indicates the existence of residual organics. The pyrochlore-phased sample (550°C pre-annealed, without final annealing) exhibits no obvious peaks in the entire wavenumber range, whereas the annealed samples with single perovskite phase show significant peaks at 691 cm^{-1} and 524 cm^{-1} , being assigned to Ti-O bonding in perovskite structure [19].

Figure 3.10 XRD patterns of samples at different processing steps.

Figure 3.11 FT-IR spectra of samples at different processing steps.

3.3.3 Microscopic Morphologies

FE SEM micrographs of PZT films pre-annealed at 550°C and 600°C are shown in Figure 3.12 (a) and (b), respectively. The surface morphologies reveal a typical ‘rosette’ structure [56], featuring many randomly scattered circular zone of coarse-grain and surrounding fine grain area. The fine grain size is about 10 nm. From the XRD patterns in section 3.3.2, it can be concluded that both coarse grains and fine grains are of perovskite phase. It is also obvious that there is a larger portion of rosettes in Figure 3.12 (b) than that in Figure 3.12 (a), indicating that, with increasing pre-annealing temperature or annealing time, the coarse-grain rosettes grow radially until they meet each other.

(a) pre-annealed at 550°C

(b) pre-annealed at 600°C

Figure 3.12 Surface morphology of sol-gel derived PZT thin film.

Chapter III Deposition of PZT films on silicon using hybrid processing technology

Microcracks with a length of several microns are easily found at inter-rosette boundaries in the 600°C pre-annealed sample (Figure 3.12). Nevertheless, as the stress being relaxed through micro-cracking, the possibility of macro-cracking would be very low. This is confirmed by a microscopic examination of the two samples. No macro-scale cracks are found in the 600°C pre-annealed sample, whereas in the 550°C pre-annealed sample, macro-cracks of several millimeters long are easily found even before final annealing. This can be attributed to the weak strength of the film before perovskite structure formed. The higher the portion of well-crystallized perovskite structure, the higher the strength of films, thus the lower the probability of cracking. Based on the above discussion, it is concluded that, (a) macro-scale cracking is easily found in amorphous or pyrochlore phased films (550°C pre-annealed sample before final annealing); (b) the well-crystallized perovskite structure prevents the film from macro-cracking; (c) by raising the pre-annealing temperature or time the probabilities of cracking can be minimized.

Figure 3.13 The cross section of PZT film pre-annealed at 550°C.

Figure 3.14 The cross-section of PZT film pre-annealed at 600°C.

Figures 3.13 and 3.14 show the cross-sections of the films revealed by fracturing two samples (5 layers, pre-annealed at 550 °C and 600 °C, respectively). The thickness is measured as 0.8 μm , and no distinct interface or pores are found between multiple layers. This means that, after final annealing at 650 °C for 20 minutes, the columnar grains have been well developed throughout the whole film thickness, resulting in a dense and uniform microstructure.

3.3.4 Dielectric and Ferroelectric Properties

For electrical characterization, 0.8 mm $\times$ 0.8 mm platinum top electrodes are deposited onto the surface of the films by a shadow masking method. The exact areas of electrodes are determined using an optical microscope and a calibrated graticule. The bottom platinum electrode is revealed by etching away a corner of the film in a chemical solution of HCl/HF/H₂O with a volume ratio of 50:0.1:50.

Dielectric measurement is carried out using an HP 4284 precision LCR meter (100 Hz to 1 MHz, 50 mV). Figure 3.15 shows frequency dependence of dielectric property of the element. Dielectric constant ϵ_r is about 1100 with slightly descending frequency dependence as frequency increases.

Dielectric loss D remains flat below 0.1 in the frequency range of $1 \sim 10^5$ Hz.

Figure 3.15 Dielectric properties of a 1.1 μm thick PZT thin film sample.

In general, the dielectric loss arises from two mechanisms: conduction loss and relaxation loss [57]. In our case, conduction loss is the dominant mechanism, where the dielectric loss is due mainly to the defects in the film. The lower dielectric loss indicates low defect densities in the film. When annealed at higher temperature, the film is better crystallized, and the defects density in the film is reduced. However,

higher annealing temperature may induce other problems, such as the reaction of PZT films with the bottom electrodes, the peeling off of the films from the substrates, and incompatibility with other MEMS processes. As our major aim is to develop an IC compatible technology for depositing PZT onto silicon wafers, a compromise has to be made. Finally we choose a relatively lower annealing temperature of 650 °C, where the perovskite structure of PZT is just well-developed and a relatively low dielectric loss is achieved.

Precision Pro material analyzer is used to measure the P - E hysteresis loop of single transducer element. The results for a 1.1 μm thick PZT thin film sample are presented in Figure 3.16. The remanent polarizations P_r and coercive field E_c are measured as 15.5 $\mu\text{C}/\text{cm}^2$ and 31.5 kV/cm, respectively. The ‘thin’ loop indicates the ‘soft’ nature of the piezoelectric film, which indicates that the orientations of the domain polarization are easily reversed.

Figure 3.16 P - E hysteresis loop of a 1.1 μm thick PZT thin film sample.

3.4 PZT thick film deposition using novel hybrid processing technology

As mentioned in Chapter 2, there exists a thickness gap in the PZT film deposition technology. 0.5~2 μm thick PZT thin films can be realized by methods such as sputtering, pulse laser deposition, chemical vapor deposition, sol-gel, and are useful for the application of microelectronic and MEMS sensing devices; whereas the ‘thick’ film fabrication usually employs the techniques such as screen-printing and tape casting. For applications such as ultrasonic transmitters and high-force actuators, dense, crack-free PZT films of 2~50 μm thick are usually required to produce a high output power or a large generative force.

For deposition of PZT thick films, several technologies have been proposed: multiple coating of sol-gel layers (e.g. diol-based [58] or HAc-based sol-gel method [59]); screen printing [60]; a mixed method of thin films prepared by sol-gel routes and loaded with powder of similar composition [61]; and hydrothermal method [62]. Among these technologies, screen printing is presently the only practical method for thickness larger than 10 μm , but it requires high temperature sintering, which is not desired in MEMS processing. The powder loaded sol-gel process has received more attention for its simplicity and producibility. Sayer et al. [61] 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. 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 [63] and the coarse surface on the film [61]. Therefore, preparing thick uniform PZT films with large area by the sol-gel technique at low processing temperature is still challenging.

3.4.1 Experimental Procedure

The basic idea of our hybrid technology is to uniformly disperse the ceramic PZT ceramic powders into PZT sol-gel solution to form a kind of uniform slurry for further deposition onto given substrates.

3.4.1.1 Preparation of uniform slurry

Preparation of the uniform slurry for PZT thick film deposition is illustrated in Figure 3.17. Commercial PZT powder (APC850) is used as particle source to be loaded in the PZT53/47 solution. High-energy ball milling (Frisch Pulverisette 5 planetary ball milling machine) is employed to obtain the powders with desired particle size (nano-sized PZT particles). Containers and balls made of tungsten carbide (93 wt% WC + 6 wt% Co, $\rho = 14.75 \text{ g/cm}^3$) are chosen for the chemical inertness, high stiffness and high density of the material. It is shown that the commercially available PZT powder had a wide distribution of grain size and most of them are above $0.5 \text{ }\mu\text{m}$. A small amount of the powder exhibits a spherical morphology while the most other particles show irregular morphologies with sharp facets. After dry milled at 200 rpm for 32 hours, the raw powder particles are smashed into a

smaller size. The average particle size estimated from the FE-SEM images is about 20 nm, which is much smaller than that of the raw powders, and has a nearly spherical shape. Therefore, by using the high energy ball milling process, we can achieve much enhanced uniformity of the PZT slurry.

Figure 3.17 Flow chart for preparation of PZT slurry.

However, as the average powder size shrinks, the powder becomes easily subject to agglomeration. To overcome this problem, a selected dispersant (organic vehicle) is

added into the milled powders and ball milled for 12 hrs. This process actually serves as a surface modification of the powder. 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 behavior in order to break down the agglomerates during the processing.

After dry milling, PZT sol-gel solution prepared (in section 3.3) is then added to the ceramic powder for wet milling at 150 rpm for 12 hrs. In this way, uniform PZT slurry is achieved and ready for further deposition processing, such as spin coating, tape casting, screen printing, etc.

3.4.1.2 Deposition of PZT thick films on platinized silicon wafers

The as-prepared PZT slurry is then deposited on silicon wafers by spin-coating. The multiple coating procedures are similar to that of the sol-gel deposition described in section 3.3.

Before the PZT composite film deposition, a pure sol-gel layer is 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 completes the deposition. A pure sol-gel layer after every 3 composite layers deposition or less can also enhance the internal density. The sol-gel solution can infiltrate into the pores in the ceramic powder derived PZT phase.

3.4.2 Phase Identification

All x-ray diffraction patterns of the PZT films annealed in the temperature range of 600-700 °C show single-phase perovskite peaks and no observable second phase within the detection limit of the x-ray diffraction. Figure 3.18 shows clearly the single-phase perovskite structure characterized by peaks at 21.9° (100), 31.0° (110), 38.2° (111) and 44.6° (200).

Figure 3.18 Typical XRD pattern of PZT thick film sample fabricated by hybrid processing.

3.4.3 Microscopic Morphologies

Figure 3.19 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 is 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 is 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 dense microstructure. Excellent adhesion occurs between the ceramic films and the underlying platinum-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, certain 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.

Figure 3.19 FE-SEM images of PZT thick films (4012) derived from slurry loaded with nano-sized particles. (a) Cross-section; and (b) surface morphology.

3.4.4 Dielectric and Ferroelectric Properties

Figure 3.1 shows the frequency dependence of relative permittivity ϵ_r and dielectric loss D for (4013) PZT composite thick films on platinum-coated silicon substrate. The measurement is carried out ranging from 100 Hz to 1 MHz at 50 mV using an HP 4284 precision LCR meter.

The relative permittivity ϵ_r is 1115 and dielectric loss D is 0.009 at 1 kHz. Compared with those of HAc-sol-gel-derived PZT thin films, the permittivity is about the same, while the dielectric loss is much lower.

Figure 3.10 Frequency dependence of dielectric property at room temperature for PZT composite thick films (4013) derived from nano-sized particle loaded slurry.

Generally, the main influential factor responsible for the dielectric loss may be the porosity that originates from organic evaporation and agglomeration. For PZT thin

film prepared by pure sol-gel method, pin-holes in the films seem to be inevitable due to the removal of substantial amount of organics. The presence of these defects will lead to increased dielectric loss. While in the case of thick films derived from slurry loaded with nano-sized particles, since the porosity is remarkably decreased and microstructure is dense in films, the dielectric loss has been substantially decreased.

Figure 3.21 P - E hysteresis loop of PZT thick films (4013) on Pt/Si substrate derived from slurry with nano-sized particle loaded.

Figure 3.2 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 $42.3 \text{ kV}/\text{cm}$, respectively. The P_r is lower than that of PZT thin films, while the coercive electric field is higher. Since the coercive field E_c refers to the field value required to reverse the direction of the domain by definition, larger E_c indicates that domain reversal in PZT composite thick

films from nano-sized particles becomes difficult. The relatively lower P_r is attributed to the degraded ferroelectric properties of nano-size PZT powders prepared by high-energy ball-milling method.

3.5 Summary and conclusions

In this chapter, three kinds of sol-gel routes are studied. Some related kinetic parameters of phase formation are calculated using Kissinger's method. It has been found that three kinds of reactions, pyrochlore crystallization, de-oxygen, and perovskite crystallization, make up the whole process of perovskite formation. The effective activation energies of each reaction are calculated as 52.6, 246.7, 74.2 kJ/mol for acetic acid gel, and 457.2, 68.1 kJ/mol for MOE gel. Acetic acid has an advantage over MOE as solvent, for its low activation energy required for phase transition. A PZT thin film deposition method is developed based on a modified acetic acid route, enabling PZT thin films with thickness less than 2 microns to be deposited on silicon substrate. Macro-scale cracks are avoided by introducing a pre-annealing step. Being finally annealed at 650°C for 30 min, the films show single phase of perovskite, and exhibit good ferroelectric properties. The remanent polarizations P_r and coercive field E_c are measured as 15.5 $\mu\text{C}/\text{cm}^2$ and 31.5 kV/cm for a typical 1.1- μm -thick PZT thin film sample. A hybrid deposition technique is presented. PZT thick films ranging from several microns to 20 microns are successfully fabricated onto silicon substrate. Phase formation, microstructure, dielectric and ferroelectric properties for these PZT thin/thick films are characterized. 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.

CHAPTER FOUR

PIEZOELECTRIC CHARACTERIZATION OF PZT FILMS USING A NOVEL SCANNING INTERFEROMETER

4.1 Introduction

This chapter devotes to the development of a modified scanning Mach-Zehnder interferometer and the scanning interferometric method for piezoelectric characterization of PZT films.

As mentioned in Chapter 2, a novel method for piezoelectric thin film characterization using a commercially available laser scanning vibrometer (LSV) has been proposed and demonstrated by K. Yao et al. [32]. It can be expected that these scanning laser interferometric systems would become promising tools, as a

replacement for current single-point interferometers, for piezoelectric measurement of thin films as well as for vibration measurement of various MEMS devices. However, the commercial LSV measures directly the vibration velocities rather than displacements, and the accuracy is degraded as the vibration frequency increases. At present, the bandwidth of the commercially available LSV is limited by the frequency difference of heterodynes, i.e., usually 40 or 80 MHz. In the actual measurement, as the sampling rate should be high enough to achieve desirable accuracy, the maximum operating frequency for the heterodyne vibrometers is actually much lower than the frequency difference.

Based on a novel modulation technique [64], we have successfully developed a scanning homodyne interferometric system [65] that has achieved a high resolution down to the picometer range as well as a much enhanced bandwidth. The main advantageous features of the homodyne interferometer over the commercial heterodyne vibrometers include its ultrahigh resolution and the frequency independency of both resolution and accuracy. The upper bandwidth limit is determined by the response time of the photodetector (<1 ns) and the bandwidth of signal processing electronics. Therefore, homodyne interferometers have the potential to be used for high frequency applications, such as the vibration measurement of ultrasonic transmitters that work at several hundred MHz.

By employing the novel scanning characterization technique, some piezoelectric thin/thick film samples have been characterized with enhanced accuracy and consistency compared with single point measurements. The effect of several

processing parameters on the piezoelectric properties of thick films has also been discussed.

4.2 A novel scanning homodyne interferometer with pico meter resolution

4.2.1 Basic principle of homodyne interferometry

For a monochromatic laser of wavelength λ , the interference light intensity at the detection point is

$$I = \frac{1}{2}(I_{\max} + I_{\min}) + \frac{1}{2}(I_{\max} - I_{\min})\cos(2\pi\Delta x / \lambda) \quad (4.1)$$

where $I_{\max}$ and $I_{\min}$ are the maximum and minimum interference light intensity which can be measured from the interference intensity curve conveniently and Δx is the optical path-length difference between reference and probing beams. As shown in Figure 4.1, the intensity of the interference fringes varies sinusoidally with the optical path-length difference. By counting the number of intensity cycles at the photo detector, the interferometer measures how far the object has moved, in increments of $\lambda/2$. The displacement resolution can be further improved to several nanometers by using a phase multiplier circuit.

However, in piezoelectric thin film characterization, the vibration or displacement to be measured is so small ($1\sim 10^{-4}$ nm) that the induced optical path length change is far less than a wavelength. Modified interferometry has been established on the principle that the light intensity at a certain point of an interference fringe changes linearly with the alteration of optical path length difference, provided the alteration is small enough. The sensitivity of this interferometry is dependent on the optical path length difference, ranging from the theoretical maximum sensitivity at the $\lambda/4$ position to zero at 0 or $\lambda/2$ position, where λ is the wavelength of the laser source.

Figure 4.1 Schematic curve of light intensity versus optical path-length difference when interference occurs.

For a small displacement much less than a wavelength ($<10 \text{ \AA}$), at the $\lambda/4$ point, the interference intensity change detected at the photodetector is linearly proportional to the displacement, and is given by:

$$\begin{aligned} I &= \frac{1}{2}(I_{\max} + I_{\min}) + \frac{1}{2}(I_{\max} - I_{\min})\sin(4\pi\Delta d / \lambda) \\ &\approx \frac{1}{2}(I_{\max} + I_{\min}) + \frac{1}{2}(I_{\max} - I_{\min})4\pi\Delta d / \lambda \end{aligned} \quad (4.2)$$

where Δd is the displacement of the vibrating object. The light intensity is converted into current by a photodetector, and further transformed to a voltage by a current preamplifier. For a given periodical displacement with amplitude of d_0 , the detected voltage signal also takes a sinusoidal form with amplitude of V_{out} corresponding to the displacement amplitude d_0 , and can be expressed as:

$$d_0 = (\lambda/2\pi) \cdot (V_{out}/V_{p-p}) \quad (4.3)$$

where V_{p-p} is the peak-to-peak voltage corresponding to the interference signal ($I_{\max} - I_{\min}$). Both V_{out} and V_{p-p} can be measured directly from a dynamic signal analyzer or from a lock-in amplifier, and the displacement of the vibrating object can be calculated from equation (4.3).

However, the optical path length difference is subject to environmental factors such as air flow and temperature change, which cause the fringes to move randomly, so that stable sensitivity cannot be easily achieved under the normal laboratory conditions. This problem is commonly solved by using a feedback technique of actively fixing the optical path length difference of the interferometer arms at the most sensitive position, the so-called $\lambda/4$ condition using a moving mirror actuated by

a piezoelectric or electrostrictive actuator. To provide this adjustment the reference mirror is mounted on a piezoelectric or electrostrictive actuator. The actuator is driven by a closed loop servo system which monitors the dc output from the detector preamplifier and applies the necessary voltage to the actuator to hold the optical path length difference to $\lambda/4$. The actuator is also used to calibrate the interference signal. Before an experiment is performed the actuator is driven with an ac signal sufficient to create a full fringe shift. By this method the change of light intensity corresponding to a full fringe shift (a displacement of $\lambda/2$) is determined as a peak-to-peak voltage V_{p-p} by the photodetector. After this measurement the servo system is activated to fix and hold the interferometer at the $\lambda/4$ condition for small vibration measurement. The piezoelectric displacement is determined by comparing the detected signal V_{out} with the peak-to-peak voltage V_{p-p} .

This ordinary technique of feedback servo suffers from a rather complicated servo system, which includes at least a differential amplifier, a low-pass amplifier and a servo amplifier. Moreover, the calibration can only be done before the actual vibration measurement, making the measurement less reliable when intensity drift occurs during the measurement. This is the major obstacle for these homodyne interferometers used for scanning applications. One can imagine if the measure point is shifted from one position to another of the sample, the inhomogeneous reflectance of the sample surface may cause the intensity change of the probing beam, and a recalibration has to be carried out to ensure the accuracy. Therefore, it is not convenient for the feedback-servo-based homodyne interferometers to be used in an automatic scanning setup.

In order to overcome the above mentioned difficulties, a modulated laser interferometer is proposed and realized to solve the random drift problem of the fringes caused by the environment or even the intensity variation of the laser source. The optical path-length is altered by the actuator to pass across the $\lambda/4$ point periodically rather than to be fixed at $\lambda/4$ point. A modulated V_{out} signal is thus obtained and both the amplitude and the phase of the vibration can be easily determined without the complicated closed loop servo system. The modulation technique enables a self-calibration to be carried out concurrently with each measurement. The accuracy is thus maintained when measured point of the sample moves from one position to another.

In our system, automatic scanning is achieved by moving the sample through PC-controlled X-Y motorized stages. This scanning interferometric system outperforms the commercial SLDV in several aspects such as high resolution down to the picometer range and much enhanced bandwidth.

4.2.2 System configuration

Figure 4.2 shows the optical setup of the scanning homodyne interferometric system.

Figure 4.2 Optical setup of the scanning interferometer.

The scanning Mach-Zehnder interferometer schematically showed in Figure 4.2 is based on the same principle of high-resolution homodyne Mach-Zehnder interferometers [27-31]. The laser beam emitted from the laser source (Melles Griot He-Ne, Intensity & Frequency Stabilized) passes through an optical aperture, which is

to prevent the back reflection into the source. The beam splitter (BS1) reflects the horizontally polarized parts of the laser beam into the reference arm while it lets the vertically polarized parts to pass through as the probing arm. After passing another beam splitter (BS2), the probing beam reaches a properly aligned quarter-wave plate. The polarization orientation of the passed probing beam is rotated for 45° by the quarter-wave plate. The beam is then focused by a lens onto the front face of the sample and is reflected back to pass through the $\lambda/4$ plate again. In this way, the orientation of polarization is rotated for another 45° and becomes horizontal, allowing the probing beam to be reflected by BS2 to reach the mirror (M2) and then get reflected back. Meanwhile, the polarization direction is changed back to vertical by passing another $\lambda/4$ plate twice, enabling the probing beam passing through BS2 to reach the half-reflecting mirror. On the other hand, the beam traversing in the reference arm is directed towards a piezoelectric actuated mirror, and is then reflected back. After passing the quarter wave plate twice, the reference beam changes the polarization orientation to vertical and is able to pass straight through BS3 all the way to the half-silvered mirror, where the two beams are combined and interference occurs. The interference patterns are magnified by the expanding lens and projected onto the photodetector (Newport, 818-BB-21). The intensity of the interference patterns are measured by the photodetector, which can either be connected to an oscilloscope (TDS 5034) with input impedance of $1\text{ M}\Omega$ for high bandwidth (up to 350 MHz) measurements, or be connected to a lock-in amplifier (EG&G 5302) for high resolution (1 pm) measurements.

The half-wavelength plate between M1 and BS1 is introduced to control the intensity ratio of the probing beam to the reference beam. When the reflectance of the sample surface is averagely poor, we can increase the proportion of the vertical polarization by properly aligning the orientation of this plate, allowing more laser energy to be divided into the probing arm to compensate for the intensity loss on the sample surface.

The sample holder is placed on two stacked stages (PI, M-126.CG) which utilize compact closed-loop DC motors with shaft-mounted high-resolution position encoders and precision gearheads to provide minimum incremental motion of 0.007 μm and unidirectional repeatability of 0.1 μm . The X-Y stacked translation stages are controlled by a computer so that the high-precision 2-dimensional scanning can be performed according to a predetermined scanning grid or trajectory. Control software based on NI Labview has been developed for auto-scan control and data acquisition.

4.2.3 The novel modulation technique

The key component of this interferometer is the piezo-actuated mirror that provides low frequency modulation to the optical path-length of the probing beam.

In this modulation method, the actuator is driven by an ac voltage signal, preferably a triangular-shaped wave signal, and moves the mirror over a distance greater than $\lambda/2$ so that the V_{p-p} can be measured. The path-length modulation also enables the measurement condition to pass across the maximum sensitivity ($\lambda/4$ point)

periodically, thus the tested V_{out} at the maximum sensitivity is easily determined as the maximum amplitude of the voltage response.

During measurement, when the modulation is activated, the intensity of the interference patterns, which is the mixture of the object's small vibration signal and the large reference signal due to the optical path-length modulation, is measured and converted to a current signal by the photodetector. The current signal is amplified and converted into voltage signal by a current amplifier and subsequently transmitted directly to one channel and high-pass filtered to another channel of an oscilloscope or a dynamic signal analyzer. The amplitudes of the signals in the two channels, low frequency signal representing V_{p-p} and the high frequency signal representing V_{out} , can be visualized and compared simultaneously and the amplitude of the displacement can be measured.

When a triangular wave at a low frequency f_a , is applied directly to the actuator, a sinusoidal wave can be observed, provided the amplitude of the triangular wave (V_{tri}) is properly adjusted to move the reference mirror over an optical path-length of several $\lambda/2$. The peak-to-peak amplitude of this sinusoidal wave is measured as V_{p-p} in equation (4.3).

Once the driving ac voltage at a frequency f_d equal to several kilo hertz is being applied on the sample, the detected signal becomes a summation of the low frequency component and the high frequency one. If this signal is to pass a high-pass filter or notch filter at the modulation frequency, a sinusoidal modulated displacement signal

will be observed from the digital signal analyzer (shown in Figure 4.3). The sinusoidal modulation frequency, dependent on f_a as well as V_{tri} , is given as:

$$f_{\text{mod}} = f_a \cdot V_{tri} / V_{\lambda/2} = n f_a \quad (4.4)$$

where $V_{\lambda/2}$ is the voltage that moves the reference mirror for an optical path-length of $\lambda/2$. The V_{out} in equation (4.3) is thus determined as the maximum amplitude of the modulated signal, which can be readily read out from an oscilloscope or a digital signal analyzer. The environmental disturbances can only affect the position at which the maximum amplitude occurs but does not affect the amplitude value. Thus, the maximum amplitude is immune from environmental drifts and circuitry noises, and therefore, a stable measurement of V_{out} is realized.

Figure 4.3 The amplitude modulation signal of the object's small vibration measured by a digital signal analyzer after high-pass filtering.

By using a multi-channel signal analyzer or oscilloscope, we can detect two signals at the same time, one is the low frequency V_{p-p} signal without high-pass filtering, and the other is the high frequency V_{out} signal (shown in Figure 4.4). The amplitudes of the two signals are compared and the displacement is calculated from equation (4.3). Without the lock-in amplifier, a resolution down to several angstroms has been achieved.

Figure 4.4 Simultaneous measurement of V_{p-p} and V_{out} , revealing that the maximum sensitivity occurs around the $\lambda/4$ position.

For characterization of piezoelectric thin films, displacement measurement with sub-angstrom resolution is required. Generally, lock-in techniques can be used to single out the tiny signals that have been buried in the Johnson noise and $1/f$ noise, and to significantly improve the resolution down to 10^{-2} Å. In the case of the

modulation technique; however, the signal measured by photodetector takes the following form:

$$V_{\text{mod}} = \sin(2\pi f_{\text{mod}}t + \varphi_1) \cdot V_{\text{out}} \sin(2\pi f_d t + \varphi_2) \quad (4.5)$$

where f_d is the frequency of the detected small vibration. In order to detect this modulated signal by a lock-in amplifier, the driving ac source offers the reference frequency for lock-in, and a time constant much shorter than the period of modulation is chosen. In this way, a sinusoidal voltage output with frequency equal to f_{mod} and an amplitude equal to the rms value of V_{out} is obtained from the lock-in amplifier. For instance, when slow modulation (4 Hz) is used, the lock-in amplifier with a 10 ms time constant captures the details of the modulated signal very well as shown in Figure 4.5.

Figure 4.5 Lock-in measurement of V_{out} together with direct measurement of V_{p-p} ($t_c = 10 \text{ ms}$, $f_{\text{mod}} = 4 \text{ Hz}$).

The displacement versus driving voltage curve for the tested ceramic sample is shown in Figure 4.6. The peak-to-peak values of driving voltage ranged from 0.2 V to 20 V. The results indicate a very good linearity over a wide dynamic range (2 pm ~ 4 nm). The resolution is high enough for characterization of piezoelectric thin/thick films.

Figure 4.6 Displacement versus driving voltage curve for the tested sample.

It should be noted that, by using the modulation technique, a self-calibration is carried out at the same time as one measurement is made. Therefore, the measurement is neither susceptible to the laser intensity instability, nor to the roughness and reflectance changes of the sample surface. This kind of self-calibration enables fast measurements to be performed with the point of investigation moving from one position to another or from sample to sample, while maintaining accuracy.

It is thus possible to achieve automatic scanning of the sample surface for measuring the vibration modalities.

4.2.4 Discussion

For the scanning homodyne interferometer, the out-of-plane resolution is the same as that of the single-point modulated Mach-Zehnder interferometer, where picometer resolution has been demonstrated using a PZT bulk ceramic sample. Though higher than that of a heterodyne interferometer, the resolution of homodyne interferometers is strongly dependent on the laser intensity. If the reflectance of the sample surface is poor, the laser intensity loss on the surface will result in a much degraded resolution. While for heterodyne interferometers, the resolution is not so sensitive to the laser intensity, enabling these interferometers to measure over rough surfaces or over a long distance. However, for most MEMS devices fabricated on single crystal silicon substrate, the surfaces are usually smooth enough to achieve desirable resolution when homodyne interferometer is used.

In characterization of high frequency vibrating devices, e.g., micromachined ultrasonic transducers, the bandwidth of the instrument is of primary concern. Unlike heterodyne interferometers, where maximum frequency is limited by the frequency difference of heterodynes and the sampling rate, the upper bandwidth limit of the scanning homodyne interferometer is theoretically determined by the response of the photodetector. In our system, the Newport 818-BB-21 photodetector has a response

time of less than 1 ns, featuring a bandwidth up to 1.5 GHz. However, the actual bandwidth of the system is limited by the bandwidth of signal processing electronics. For measurements with lower resolution of the angstrom range, the high-pass filtered signal is directly input to the oscilloscope with input impedance of 1 M Ω . The actual bandwidth is up to 350 MHz for TDS 5034 in our system. In the case of high resolution measurement down to picometers, lock-in amplifier has to be employed, and the actual bandwidth is limited to 1 MHz for EG&G 5302. Since lock-in amplifiers working at higher frequencies are commercially available, the scanning homodyne interferometer has the potential for more improved bandwidth without degradation of resolution and accuracy.

4.3 Piezoelectric characterization of PZT films using scanning interferometric method

4.3.1 Scanning interferometric method for measurement of longitudinal piezoelectric coefficients of PZT films

With regard to the measurement of longitudinal piezoelectric coefficient for piezoelectric thin/thick films, various kinds of sensitive interferometric methods have been proposed. In order to eliminate the influence of the substrate movement, a

double-beam setup is commonly used to simultaneously detect the displacement in both the front and the back side of the piezoelectric film samples. However, the double-beam method requires critically precise optical alignment. The front probing beam and the back probing beam should be strictly aligned to the same line, otherwise the substrate bending displacement would not be completely eliminated. A novel method using a commercially available laser scanning vibrometer (LSV) has been reported by K. Yao et al. By using this scanning interferometric technique, the vibration of both the on-electrode and off-electrode areas are monitored. The displacement difference of the two areas is actually the longitudinal dilation of the piezoelectric film. This scanning method possesses several unique advantages over the single-point displacement detection methods, including easy sample mounting and fast optical alignment, high reliability and consistency. Furthermore, the data obtained by this scanning technique yield much more information than that obtained by the single-point measurement using a double-beam system. For example, the substrate deformation can be easily and accurately measured by a line scanning, which is closely related to the transverse piezoelectric coefficient (d_{31}) of the films as well as the mechanical properties of both the piezoelectric film and the substrate. Given a proper analytical model or finite element model, it is possible to use the deformation data to work out the transverse piezoelectric coefficient or other mechanical properties of the piezoelectric films.

4.3.2 Experimental

The PZT thin films under investigation are fabricated through an acetic acid based sol-gel processing on Pt/TiW/SiO₂/Si substrates by multiple spin-coating and 650 °C annealing. The thickness of the fabricated thin films is ranging from 0.4 μm to 1.1 μm. The PZT thick film samples are prepared using a hybrid sol-gel deposition method described in Chapter 3 in detail. In this method, the PZT sol-gel solutions are mixed with high-energy ball milled PZT ceramic powders to form uniform slurry. The slurry is ready for further thin film processing, such as spin-coating, tape casting, screen printing and molding. In our experiments, we deposit the prepared uniform PZT slurry on the platinized silicon wafer by spin-coating. The processing parameters are summarized below,

Spin speed at 3000 rpm;

Preheating at 250 °C and 500 °C on a hot plate;

Final annealing at 650 °C ~ 750 °C for 30 minutes in a tube furnace.

In order to evaluate the role of slurry recipe on the piezoelectric properties of the resultant thick films, samples are prepared with slurries at different sol-gel concentrations and different powder/solution mass ratios, as shown in Table 1. Furthermore, some of the samples are subjected to cold isostatic pressing (CIP) treatment to increase the density of the PZT thick films. Since the resultant films are composite and the added powder occupies the majority of the volume fraction, the performances of the resultant film are mainly determined by the properties of the

powder. Therefore, the commercially available powder should be pre-sintered at 1200-1300 °C for 30 minutes to improve its crystallinity before being mixed with precursor solution and the powder size should be in the range of 100 to 300 nm. Under the above conditions, we can conveniently control the film thickness from several microns to several tens of microns within 10 spin-coating steps.

Table 4.1 Sample numbers and the corresponding processing parameters.

Sample No.	3023	3012	3025	4023	4012	4025
Sol-gel concentration	30	30	30	40	40	40
Powder/solution mass ratio	2:3	1:2	2:5	2:3	1:2	2:5

After film deposition, rectangular Pt top electrodes (0.8mm × 0.8mm, 300 nm thick) are then deposited on the PZT films by sputtering. The bottom Pt electrodes are made accessible by etching away a corner of the PZT film. Piezoelectric characterizations are then carried out using the scanning modulated interferometer. Each sample is attached to a sample holder on PC-controlled X-Y translation stages. Scanning is achieved by moving the sample with step resolution down to 5 μm, a resolution high enough to capture the details of vibration modalities within a 0.1mm × 0.1mm area of interest. Both one dimensional and two dimensional scanning are performed for a given area that covers the dot electrode.

4.3.3 Results and discussion

A typical 2-D scanning results depicted in Figure 4.7 shows clearly the displacement distribution within the given area. There is a clear-cut displacement gap between the electrode covered area and the ambient area. This displacement gap is due to the longitudinal dilation of the piezoelectric film. Once the displacement gap is measured, the apparent d_{33} of the piezoelectric film can be simply determined by dividing the gap with the applied voltage. The spurious data at one corner are false data caused by the occurrence of the needle probe that is placed on the corner of the electrode for electrical contact. In the actual measurements of apparent longitudinal piezoelectric coefficient, considering the symmetry of the dot electrode, only 1-D scanning is carried out across the electrode.

Figure 4.7 Two dimensional scanning of the thick film sample 3025 (X,Y axis in 0.1 mm, Z axis in nm, ac driving voltage: 4Vp-p, dc bias: 30V).

4.3.3.1 Thin film characterization

The displacement distributions by coarse scanning (1~2 mm step resolution) across the whole sample and by fine scanning (0.05~0.1 mm step resolution) near the top electrode are given in Figure 4.8(a) and Figure 4.8(b), respectively. Figure 4.8(a) shows that the substrate has a rather complicated vibration modality, featuring a significant localized deformation at the position of the dot electrode. The much smaller out-plane displacement of the piezoelectric thin film can hardly be identified until a fine scanning near the electrode is performed. As shown in Figure 4.8(b), the clear-cut gap between the displacement of the substrate and that of the thin film under driving voltage is exactly the longitudinal displacement of the piezoelectric thin film that we are interested in. The maximum substrate bending displacement occurs at the center of the top electrode (see the fitted dot line in Figure 4.8(b)) and is measured as about 0.32 nm. Although the longitudinal dilatation is only 21.1% of the maximum substrate bending displacement, it is easily identified by a fine scanning with step resolution of 20 μm . The displacement measurement is carried out at different bias voltages and the apparent values of longitudinal piezoelectric coefficient (d_{33}) are calculated as the longitudinal displacements divided by the driving voltage. The d_{33} - E_{bias} loops are shown in Figure 4.9(a) and Figure 4.9(b). The maximum d_{33} values are measured as 60 pm/V and 88 pm/V, respectively, for two samples with different film thickness.

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(a) coarse scanning across the entire sample;

(b) fine scanning across the electrode.

Figure 4.8 Displacement distribution measured using the scanning interferometer.

(a) 0.5 μm sample;

(b) 1.1 μm sample.

Figure 4.9 The d_{33} versus E_{bias} loops for thin film samples with different thickness.

4.3.3.2 Thick film characterization

Theoretically, the longitudinal piezoelectric displacement of thicker PZT films are more pronounced compared with substrate bending displacement. The substrate bending is due to the transverse piezoelectric displacement, d_t , which can be expressed as,

$$d_t = d_{31}El = d_{31}Vl/d \quad (4.6)$$

where d_{31} is the transverse piezoelectric coefficient, E is electric field, V is applied voltage, l is the effective length of electrode coverage, d is film thickness.

Whereas the longitudinal piezoelectric displacement is,

$$d_l = d_{33}Ed = d_{33}V \quad (4.7)$$

therefore,

$$d_l/d_t = (d_{33}/d_{31})d/l \quad (4.8)$$

From equation (4.8) we know that the longitudinal to transverse displacement ratio is proportional to film thickness. Larger film thickness leads to higher longitudinal to transverse ratio, thus less influence of substrate bending motion. In this sense, the longitudinal piezoelectric response of thicker films is more easily measurable with this scanning method.

Figure 4.10 shows a typical example of piezoelectric displacement measurement result by line scanning across one dot electrode for thick film sample. During the measurement, a constant ac voltage of $12V_{p-p}$ superimposed on a dc bias of 60V is applied on the top electrode. Compared with Figure 4.8, the clear-cut gap between the displacement of on-electrode part and that of off-electrode area in Figure 4.10 is much more obvious than that in the thin film case. Therefore, the longitudinal piezoelectric displacement of the film is easily measured. By this method we have carried out the apparent d_{33} measurements under different DC bias voltages for a number of samples prepared by different processing. The results are summarized and compared in Figure 4.11.

Figure 4.10 Displacement distribution measured by fine scanning across one top electrode for thick film sample ($7.14 \mu\text{m}$).

(a) sol-gel solution 30%, powder/solution mass ratio 2:3/2:5;

(b) sol-gel solution 30%, powder/solution mass ratio 2:5, with/without CIP;

(c) sol-gel solution 40%, powder/solution mass ratio 2:3, with/without CIP.

Figure 4.11 Measured apparent piezoelectric coefficients as a function of dc bias for hybrid thick film samples prepared by different processing.

The samples with powder/solution mass ratio of 2/3 show the best piezoelectric properties, with the maximum apparent d_{33} about 120 pm/V. The samples with CIP treatments show slightly higher piezoelectric coefficients than those of the samples without CIP treatments, which indicates that denser films are more favorable for its higher piezoelectric coefficient. In addition, it seems that the concentration of the sol-gel solutions is not an influential factor for the piezoelectric properties of the resultant thick films.

A favorable feature of this scanning technique is that the data obtained yield much more information than that obtained by single point measurement using double-beam system. It can be obviously seen from Figure 4.8 that the displacement and the curvature of the substrate bending deformation can be easily and accurately determined by a line scanning. These data are closely related to the transverse piezoelectric coefficient (d_{31}) of the films as well as the mechanical properties of both the piezo films and the substrate. As the Young's modulus and Poisson's ratio of the silicon substrate are available, it is feasible to use the data to work out the transverse properties or the mechanical properties of the piezoelectric films, provided a proper analytical model or finite element model was established. These properties are quite essential for either material research or piezo-MEMS design.

It should be pointed out that we have assumed the deformation of the substrate outside the electrode region to be the same as that below the top electrode. According to the results of FEM analysis [66], this assumption is only valid when the size of the top electrode exceeds a critical value (around 1 mm). As the electrode dimension of our samples is 0.8 mm, this assumption would not cause an error above 5%. In addition, the FEM analysis reveals that the effective d_{33} measured directly is only about 1/3 of the d_{33} free of constraint. For example, the real longitudinal piezoelectric coefficients of the piezoelectric thin films shown in Figure 4.9 should be about 180 pm/V (0.5 μm sample) and 264 pm/V (1.1 μm sample) under optimized bias voltages.

4.4 Summary and conclusions

In this chapter, a modified scanning homodyne interferometer is successfully developed based on a novel modulation technique. Ultrahigh resolution down to picometer range is demonstrated by measuring the piezoelectric displacement of a PZT bulk ceramic sample.

A scanning interferometric method for piezoelectric characterization of PZT thin/thick films is presented. Various PZT thin/thick film samples prepared with different processing parameters are characterized using the novel scanning Mach-Zehnder interferometer. It is demonstrated that the apparent longitudinal piezoelectric displacement of the film samples can be easily identified and measured by fine scanning across the top electrode. The apparent longitudinal piezoelectric coefficients at different dc bias voltages are measured for various film samples. It is found that CIP treatment shows favorable effect on the piezoelectric properties of the PZT hybrid thick films and that the concentration of the sol-gel solutions is not an influential factor. As the data obtained comprise information of both longitudinal and transverse piezoelectric properties, it is feasible to use the line-scan data with the aid of a proper analytical model or finite element model to work out the transverse properties or the mechanical properties of the piezoelectric films.

CHAPTER FIVE

PIEZOELECTRIC MICROMACHINED ULTRASONIC TRANSDUCER ARRAY

5.1 Introduction

This chapter focuses on the design and fabrication of diaphragm-type piezoelectric micromachined ultrasonic transducer (pMUT) arrays by combining the hybrid PZT thin/thick film deposition technology described in Chapter 3 with bulk silicon micromachining technology.

Ultrasonic technologies have been widely used in distance recognition, biomedical-imaging and automotive sensing applications. Ultrasonic imaging and detecting possess several unique advantages over other techniques. The image presentation is in real time, which permits the identification and study of moving internal structures. Its non-destructive nature enables the technique to be used for in vivo imaging of tissues, and aids much of its clinical acceptance. The high-resolution 2-dimensional or 3-dimensional

ultrasonic imaging requires multiple transducer elements be integrated on one substrate with certain inter-spacing to form a transducer array. This array of transducers is properly phased to achieve high directivity as well as precise focusing of the ultrasound beam. In recent years, there is, particularly in the case of ultrasonic imaging for medical diagnosis, an evident technological trend towards further miniaturization of device size and higher operating frequencies in order to achieve higher axial or lateral imaging resolution. The conventional technology based on bulk ceramic transducers becomes increasingly difficult to meet the requirements.

Micromachined ultrasonic transducers (MUTs) represent a promising approach to ultrasound detection and generation. MUTs offer advantages of improved bandwidth, easy fabrication of large arrays with compact designs, and integration with support electronics [67–71]. These advantages, inherent in MUTs, enable revolutionary advances in ultrasonic imaging and many other promising applications, such as acoustic devices [72], low cost phase arrays in distance measurement, and simple object recognition [73]. For example, three-dimensional imaging requires 2-dimensional arrays of closely spaced transducer elements, these requirements can be easily met with MUTs. Two-dimensional transducer arrays of identical elements can be easily made with excellent reproducibility by using the micromachining technique. Because of the array structure of these transducers, groups of elements can be built up and used as a phased array. A number of approaches based on integrated circuits (ICs) manufacturing technology have been developed to manufacture capacitive MUTs (cMUTs) [70, 71]. Combining the deposition technique of piezoelectric film with IC technology further enables the construction of piezoelectric MUTs (pMUTs) [74-78]. Unlike cMUTs, which have an inevitable air gap

in the structure, pMUTs have a more robust fabrication process because of their simple structure. This is a very favorable feature of pMUTs from the viewpoint of reliability. pMUTs have been investigated for ultrasonic reception in a number of publications [73-78]. However, they have not been investigated sufficiently as a transmitter due to the difficulty in deposition of thick PZT film.

In this chapter, a new processing approach for design and fabrication of piezoelectric pMUT for transmitter application is developed. Owing to the well-established hybrid film coating technology [79] (elaborated in Chapter 3), various types of pMUTs arrays have been successfully fabricated with high yield. The performance of the prototype devices are characterized in terms of membrane deflection, emitting sound pressure, and directivity of emitting ultrasound beam.

5.2 Design and fabrication of bulk-micromachined pMUTs array

5.2.1 Design and modeling of the diaphragm-type transmitter element

The structure of the micromachined piezoelectric thin film diaphragm and its cross-section sketch is shown in Figure 5.1. 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 is deposited on Pt/Ti/LTO/Si₃N₄/SiO₂/Si wafer as the active layer. The uppermost layer is Pt/Ti top

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electrode with a layer of polyimide intervenes. The backside silicon is wet etched off till close to the SiO_2 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 5.1.

Figure 5.1 Schematic drawing of the diaphragm-type piezoelectric micromachined ultrasonic transducer element: top view and cross section view.

Table 5.1 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 μm	Active layer	Crack-free, high densities, patterning
Bottom electrode	Pt	160 nm	Electric contact	Orientation, patterning
Adhesion layer	Ti	60 nm	Prevents delamination of the electrode and PZT films	Oxidation control: avoids migration through grain of the electrodes
	LTO	250 nm		/
Membrane material	Si_3N_4	500 nm	Mechanical support, diffusion barrier and thermally insulating membrane	Stress control
	SiO_2	1.8 μm		

Commonly used ultrasonic transducer shapes include 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 [80]. In this thesis, square diaphragm shape is achieved as the active or

actuation element when the substrate is anisotropically etched by KOH. For high frequency array fabrication using DRIE bulk machining, the shape of the diaphragms is no longer limited to square. Various element shapes, e.g., circular dots and rectangular bars, are adopted in this case.

The bottom electrodes are 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 field. 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 5.1, 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 actuator applications, 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 an input pressure into charge generation.

When a system vibrates in a natural mode, the natural frequencies of different vibration modalities are determined by various boundary conditions, with which these frequencies can be solved out with logical functions. Rayleigh and Ritz [81] induced the solutions for solving the angular frequency ω_{2n} by finding the maximum strain (V_{max}) and

kinetic energy values and equating them, the resultant equation is expressed as:

$$\omega_{2n}^2 = \frac{2}{\rho t} \frac{V_{\max}}{\iint W^2 dx dy}, \quad (5.1)$$

where ρ is the density and t the thickness. W is a function of x and y , which is assumed to satisfy the necessary boundary conditions of the plate. Young [82] solved the fundamental frequency of the flexural modes of the rectangular plate clamped in all edges (isotropic membrane structure), that is expressed as:

$$\omega = 35.99 \sqrt{\frac{D}{\rho t a^4}} = 35.99 \sqrt{\frac{E t^2}{12(1-\nu^2) \rho a^4}}, \quad (5.2)$$

where a is the $x(y)$ -axis dimension of membrane, D the plate stiffness, t the plate thickness and ν the Poisson's ratio. Due to the multilayer structure of sensor chips, the composite membrane stiffness should be obtained by combining the constitutive layer's properties. Stiffness D can be expressed as $K/(1-\nu^2)$, where K is written as:

$$K = \sum_{i=1}^N E_i I_i = \sum_i E_i \int_{h_{i-1}}^{h_i} (z - z_0)^2 dz, \quad (5.3)$$

where E_i , h_i and I_i are the Young's modulus, height and the moment of inertia of i th layer, respectively. z_0 is the position of neutral plane, which can be expressed as:

$$z_0 = \frac{\sum_{i=1}^N E_i \int_{h_i}^{h_{i+1}} z dz}{\sum_{i=1}^N E_i t_i}, \quad (5.4)$$

where t_i is the thickness of i th layer.

The relations between stress, stiffness and membrane deflection effects on the resonant frequencies have to be considered. Firstly, the influence of stiffness variations can be expressed as the relations of stress and modulus, which have usually been used in the estimation of Young's modulus of thin film. The load–deflection method is a well-known method for the measurement of the elastic properties of thin films.

Schneider et al. [83] presented an analytical solution for the load–deflection of square membranes, which yield the relations between the acoustical pressure and the membrane deflections that makes it possible to determine the residual stress and Young's modulus of thin films. The load–deflection behavior is expressed as [83, 84]:

$$p(d) = C_1 \frac{t\sigma}{a^2} d + C_2(\nu) \frac{tE}{a^4} d^3, \quad (5.5)$$

where p is the applied pressure, d the center deflection of isotropic membrane, a one half of the membrane's edge length, t the thickness, σ the residual stress, ν the in-plane Poisson's ratio. C_1 and $C_2(\nu)$ are the numerical constants, which are determined by the results of σ and E . When the applied pressure is known, the Young's modulus can be represented by the relation of stress and dimension as given by:

$$E = C_3 \frac{a^2 \sigma}{d^2} + C_4 \frac{a^4}{td^3}, \quad (5.6)$$

where C_3 and C_4 are the numerical constants.

The equation (5.6) shows that, when the external pressure is known as a constant, the

Young's modulus or the residual stress of the membrane can be formulated from equation (5.6) using other parameters (membrane deflection, dimension) that are easy to measure.

5.2.2 Design of ultrasonic transducer array layout

An ultrasonic transducer array consists of multiple piezoelectric elements separated by a finite distance (inter-element spacing). The most advantageous feature of this transducer array over the conventional single element is its flexible beam control ability. By properly adjusting the phase of every element, a steered or focused beam can be achieved. When all the elements are set in the same phase, highly directional ultrasound beam is obtained normal to the array plane. Sharp, directive ultrasonic beams have found a lot of applications such as 2-dimensional imaging and object detecting.

Directivity of any arrangement of array is theoretically derived using Huygens' principle as follows: For a given transducer array, the ultrasound wave at a given position (polar coordinate: ρ, φ, θ) sufficiently far away from the array should be a summation of all the sub waves generated from every single array element. In the same manner, for a given single element emitting ultrasound wave, every point on the element can be considered as a sub wave source, according to Huygens' Principle. Therefore, at the given position, the ultrasound wave generated from the element should also be a summation of all the sub waves generated from every single point on the element. All this can be expressed mathematically as presented in equations (5.7) and (5.8).

$$F(\theta, \phi) = \frac{1}{N} \sum_{i=1}^N |f_i(\theta, \phi)|, \quad (5.7)$$

where

$$f_i(\theta, \phi) = \frac{1}{a^2} F_0 \cos \vartheta \int_{y_i-a/2}^{y_i+a/2} \int_{x_i-a/2}^{x_i+a/2} e^{(jk\rho \sin \theta \cos(\phi-\psi))} dx dy, \quad (5.8)$$

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

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

Sharpness of the directivity is almost in proportion to the ratio of the size of array to the wavelength, and large spacing between adjacent elements makes large side lobes when the wavelength is fixed [49]. Furthermore, a ring array is slightly more efficient than a matrix array in the meaning of directivity to the same number of elements [50].

Fundamental design parameters for an ultrasonic transducer array include:

a) Frequency (f): generally the resonance frequency of the diaphragm structure, which is dependent on the structure geometry, and mechanical properties of materials.

b) Number of elements (N): determines the directional property of ultrasound transmission and reception.

c) Inter-element spacing (d): closely related to the spatial characteristics of the sound beam. Usually d is equal to or less than half wavelength of the generated or received

ultrasound.

d) Element size of width (a): determines the operating frequency and output power.

The larger the array elements, the better the signal-to-noise ratios.

For instance, when the array is expected to be working at a frequency of around 100 kHz, corresponding to an in-air wavelength of 3.4 mm, the inter-spacing is thus calculated as $d = 1.7$ mm, and the width of squared elements can be ranging from 0.5 mm to 2 mm.

pMUT arrays with various element sizes, inter-element spacing and number of elements have been designed and fabricated. They are to be operated at different frequencies for different applications. Three typical array layout designs are presented below:

Figure 5.2 A 37-element ring array working at around 100 kHz for the application of ultrasonic speaker (square element size: 1.5 mm, inter-element spacing: 1.7 mm).

(a) 6×6 square array (0.4 mm × 0.4 mm)

(b) 16-element linear array of rectangular bars (1 mm × 0.2 mm)

Figure 5.3 Closely spaced pMUT arrays (inter-element spacing ≤ 0.2 mm) working at near 1 MHz for ultrasonic imaging.

5.2.3 Process development

The fabrication process of the micro-machined pMUTs array shown in Figure 5.4 includes steps as follows:

(a) A 4"-inch pure silicon wafer or silicon-on-insulator (SOI) wafer is dry-oxidized on both sides to form SiO_2 and Si_3N_4 insulator layer on the front surface for etching stop as well as to form mask layer for anisotropic etching on the rear surface. (b) Titanium and platinum thin layers are deposited on the front surface by sputtering and are patterned by lift-off to form the bottom electrode. (c) Silicon dioxide layer on the rear surface is patterned to make windows aligned to the diaphragm pattern on the front surface. (d) Bulk silicon is anisotropically wet-etched using KOH or dry-etched by deep reactive ion etching (DRIE) to form thin diaphragm structures. (e) Piezoelectric PZT thin film is deposited on the front surface by spin-coating, and is then patterned by wet etching ($\text{HCl}:\text{H}_2\text{O}:\text{HF}=25:25:0.1$) to expose bottom electrodes for electrical contact. (f) Insulating layer of polyimide is coated and patterned in order to prevent short circuit between top and bottom electrodes as well as to reduce parasitic capacitance. (g) Top electrode of platinum film is deposited by sputtering. And (h) a further step of DRIE is carried out to etch the silicon diaphragm to desired thickness.

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Figure 5.4 Fabrication process of pMUTs array.

With regard to the fabrication process, several aspects need to be highlighted:

a) 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 [85]. 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 is deposited on top of Si_3N_4 . Following the usual practice, titanium is chosen as the buffer layer between the oxide and platinum because direct deposition of Pt on Silicon wafer will easily result in peeling off. The buffer layer provide better lattice bond with substrate than those noble metal layers do.

As in our array layout design, the bottom electrodes define the actual transducer elements, patterning of the bottom Pt layer is thus the appropriate step. Typically, the Pt on substrate can be patterned by two ways. The first one is lift-off technique, i.e., to deposit Pt on the substrate coated with patterned photoresist layer. By subsequent removal of the photoresist layer, desired Pt pattern can be achieved. This technique is applicable for device size larger than tens of microns. 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. 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 [87, 90].

In our case of transducer array design, the element size ranges from sub millimeters to several millimeters. Therefore, the lift-off technique is chosen for patterning the bottom and top electrodes. AZ9260 photoresist layer with thickness of 10 μm is spin-coated on the substrate for electrode patterning. The Pt/Ti layer is then deposited by sputtering. After the removal of the photoresist by acetone, the well defined electrode patterns on LTO/ $\text{Si}_3\text{N}_4/\text{SiO}_2/\text{Si}$ are achieved, as shown in Figure 5.5.

Figure 5.5 Patterned Pt/Ti bottom electrode layer on the substrate by lift-off process.

b) Back side etching

The diaphragm structure is obtained by silicon bulk micromachining in hot KOH. A stress compensated bilayer of thermal oxide (SiO_2) and LPCVD nitride (Si_3N_4) is applied as the mask layer. The first lithographic step is 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 is carried out on a Karl Suss MA6 double side aligner. The KOH solution is mixed to a ratio of 44 g potassium hydroxide crystals to 100 ml de-ionized water and heated to 80°C . The samples are given a 30 seconds dip etch in 7: 1 buffered HF (BHF) to remove any native oxide prior to etching. This dip is 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 is checked every 1 hour using a surface profilometer.

Figure 5.6 Anisotropic wet etching of (100) silicon: the slowest etch rate in the $\langle 111 \rangle$ direction and the fastest in the $\langle 100 \rangle$ direction.

As shown in Figure 5.6, because the etching rate of $\langle 100 \rangle$ direction is 400 times faster than that of $\langle 111 \rangle$ direction, the etching is virtually limited by planes with minimal etching rate $\langle 111 \rangle$. A well-defined rectangular etching hole is thus obtained.

SEM images in Figure 5.7 and Figure 5.8 give the cross-section and top-view of resultant silicon membrane. The silicon left is 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.

Figure 5.7 Cross-section of a 20 μm thick wet-etched silicon membrane structure.

Figure 5.8 Top view of a silicon cavity array.

All the transducer elements fabricated through wet etching of Si substrate possess square membrane shape, due to the limitation of anisotropic etching in diamond-cubic silicon.

In the case of high-frequency (>1 MHz) pMUT array fabrication, the inter-element spacing is designed to be less than 0.2 mm. Wet etching is thus not applicable. Instead, deep reactive ion etching (DRIE) is employed to create the closely-spaced rectangular bars. Figure 5.9 shows an example of high aspect ratio DRIE micromachining.

The top view of bulk silicon micromachining by DRIE for a linear rectangular bar ($1\text{ mm} \times 0.2\text{ mm}$) array is shown in Figure 5.10.

Figure 5.9 Cross-section of a silicon wafer micromachined by DRIE, vertical walls can be achieved with high aspect ratio ($> 10:1$).

Figure 5.10 Bulk silicon micromachining by DRIE for a linear rectangular bar (1 mm $\times$ 0.2 mm) array.

c) PZT film patterning

The PZT films are deposited using the hybrid PZT coating technology which is described in detail in Chapter 3. After the PZT film deposition, it has to be etched to certain patterns so that the bottom electrode can be exposed for electrical contact with driving electronics. Lithography and etching are the key steps to define the pattern of the PZT films. 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. [86], diluted 10: 1 HF solution is 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 is employed. Moreover, hexamethyldisilazane (HMDS) is used to promote adhesion between photoresist and underlayer during lithography.

There are two approaches to pattern the PZT film: dry etching and wet etching. For the first one, reactive ion etching (RIE) using capacitive [87], inductive [88], or electron cyclotron resonance (ECR) plasma [89, 90] has been utilized to pattern PZT films. These studies are driven primarily by ferroelectric memory applications. The film thickness in these applications generally does not exceed 250 nm. Therefore, the above mentioned methods are not suitable for etching PZT films for MEMS applications which require 2 to 20 μm thick PZT films.

With regard to wet etching, three wet etching recipes, 0.34%HF: 5%HCl: 94.66%H₂O at room temperature, HF at room temperature and HCl at 45 °C, are usually adopted to etch PZT ceramics [91]. To provide a residue-free surface, good selectivity, and limited undercutting for thick film PZT patterning, L.P. Wang et al. [91]. has successfully developed a two-step etching process as shown in Table 5.2. In the first step, 10:1 buffered HF is 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 µm/min), high selectivity with respect to photoresist, and limited undercutting (2:1 lateral: thickness) are obtained. 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. Therefore, we chose the 50:50:0.1 HCl: H₂O: HF chemical solution as the etchant recipe. The etching rate at room temperature is about 0.8 µm/min. The formation of whitish residue during PZT film etching is depressed by rinsing and nitrogen drying the wafer every two minute during etching.

Table 5.2 Two-step etching process for thick PZT film patterning [91].

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

d) The use of SOI wafers

In the design of pMUT array for the application of ultrasonic speakers, the element size and the number of elements have to be increased to achieve desirable output sound power. As a result, the whole array will occupy a much enlarged area on the silicon wafer. In this case, it becomes increasingly difficult to maintain uniform thickness of the SiO₂ diaphragm throughout the whole array during back side wet etching. Consequently, the fabricated arrays may not show desirable directivity patterns because the resonance frequencies of each element within one particular array may slightly differ from each other. This problem can be solved by making use of SOI wafers, which has a one-micron-thick etching-stop layer of SiO₂ sandwiched between a silicon wafer and a thin silicon structural layer. When doing the back side etching, the wet etching process is virtually stopped by the sandwiched SiO₂ layer. So the thickness of the diaphragm is exactly the thickness of the thin silicon structural layer, and thus no longer affected by the etching process. In this way, a very uniform diaphragm thickness can be achieved throughout the whole wafer.

Figure 5.11 shows an example of fabricated pMUT arrays on a 4-inch SOI wafer for the application of ultrasonic speaker. The individual devices are separated by wafer dicing and are then connected to connectors by wire bonding. Figure 5.12 shows the front view and rear view of an as-fabricated 37-element ring array.

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Figure 5.11 Piezoelectric ultrasonic transmitter arrays fabricated on a 4-inch silicon wafer and separate array devices after wafer dicing and wire bonding.

Figure 5.12. Front view and rear view of 37-element pMUT ring array.

The schematic cross-section of a fractured transducer element is shown in Figure 5.13. The laminated layer structures can be clearly seen, in accordance with the schematic sketch of Figure 5.1.

Figure 5.13 The actual FE SEM photo of the cross section of a completed piezoelectric diaphragm-type ultrasonic transmitter.

5.3 Characterization of prototype devices

5.3.1 Measurement of membrane deflection and frequency response using interferometric method

In characterization of single transducer element, an ac voltage with a dc bias superimposed is applied on the electrodes of the transducer element to set the membrane

into vibration. The dc bias voltage presets the polarization state of the PZT film. The vibration amplitude distribution of the transducer element is measured by using Polytec PSV-300 scanning laser Doppler vibrometer (SLDV). Figure 5.14 shows a typical 3-dimensional view of the measured piezoelectric response of a square membrane at a frequency much lower than the resonance frequency. The maximum displacement amplitude at the center of the diaphragm is about 10 nm. At resonant frequency of the compound membrane, the measured displacement at the center of the membrane can reach several micrometers. This implies that the pMUT array can generate large vibration amplitude and higher sound pressure as well.

Figure 5.14 Deflection of a p-MUT element in response to an ac driving voltage measured at maximum amplitude by scanning laser Doppler vibrometer.

In order to characterize the response of the transducer array as a whole, all the array elements are connected in parallel by wire bonding, and are driven by a biased ac voltage at a certain frequency. The measured vibration distribution is shown in Figure 5.15. All the elements are vibrating with approximately the same amplitude and well in the same phase.

Figure 5.15 2-dimensional scan of a 7-element ring array with element size of 0.5 mm and inter-element spacing of 1.7 mm (3D view and top view).

To evaluate the dynamic response in a wide frequency range, frequency-scan mode of the SLDV is employed to characterize the vibration modalities of the diaphragm structure of a single transducer element. The results of this measurement for square diaphragm with element size of $2\text{ mm} \times 2\text{ mm}$ are presented in Figure 5.16. Three evident vibration modes are detected, i.e., the fundamental at 41.63 kHz, 2nd harmonic at 118.5 kHz and 3rd harmonic at 146.8 kHz.

Figure 5.16 Vibration modalities measured by scanning laser Doppler vibrometer for a 2 mm × 2 mm pMUT element.

It is known from equation (5.2) that the fundamental resonant frequency for the clamped plate model is inversely proportional to a^2 (a , the side length of the rectangular membrane). This is verified by frequency sweep measurement of the piezoelectric response at the center of the diaphragm for pMUT elements with different sizes. The results are plotted against $1/a^2$. A linear relation is obtained, as shown in Figure 5.17.

Figure 5.17 Linear relation between the fundamental resonant frequency and $1/a^2$.

In addition, the effect of dc bias on the resonance frequency is also investigated. A very narrow frequency sweep is performed as the bias voltage is varied. One of the results is given in Figure 5.18. When a dc bias voltage is added to the driven signal, the resonant frequency is shifted to higher frequencies. This is due to the piezoelectric stiffening of the PZT layer when a dc bias is applied. In other words, the applied bias indeed increases tensile stress that stretches the membrane, and thus causes the frequency increase.

Equation (5.2) is based on a model of clamped rectangular plate free of stress. When there is residual stress in the membrane, equation (5.2) can be modified as below,

$$\omega = 35.99 \sqrt{\frac{(E + T)t^2}{12(1 - \nu^2)\rho a^4}}, \quad (5.9)$$

where the stress T is added to the elastic modulus E . This equation predicts that the existence of stress in the membrane will slightly increase the resonant frequency.

Figure 5.18 Resonant frequency vs. dc bias voltage (for $1.5 \text{ mm} \times 1.5 \text{ mm}$ element size).

Figure 5.18 also shows a hysteresis characteristic of the resonant frequency versus dc bias relation, which is obviously resulting from the ferroelectric hysteresis of the PZT film. The piezo-induced stress is dependent on both the electric field and the polarization state of the PZT film. Therefore, the P-E hysteresis of the PZT film will definitely lead to similar loop in the resonant frequency versus dc bias curve.

It should be pointed out that the dc bias effect on the resonance frequency is very useful in the operation of pMUT arrays. The pMUT array has potential applications in object detection and environmental recognition due to its high directivity, both as direction finder or emitter. An electronic phased array can steer its directivity without any

mechanical scanning system. In these applications, all elements of the phased array are required to exhibit the same resonant frequency. However, the resonant frequency of each element often scatters a little due to non-uniformity of diaphragm dimensions and film thickness. The result shown in Figure 5.18 provides an approach for tuning the resonant frequency of individual element after the fabrication of the array.

5.3.2 Emitting sound pressure

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

$$SPL = 20 \log \left(\frac{P_{rms}}{P_{ref}} \right). \quad (5.10)$$

where reference sound pressure (P_{ref}) is 2×10^{-5} Pa.

By applying an ac electric voltage across the thickness of the PZT film, the lateral strain induces membrane bending; thus causes an ultrasound pressure wave to propagate in the medium in contact. The continuous ultrasound wave emitted by the transmitter is measured in air with Brüel and Kjær 2825 test system, including a 7521 signal analyzer interface module, 3016 input module, and 2670 microphone. The highest frequency of the system can reach 100 kHz. The output sound pressure level (*SPL*) of the transmitter is measured as a function of excitation frequency. An ac driving voltage of 30 V_{p-p} together with a dc bias of 20 V is applied to a 2 mm × 2 mm transmitter element. The distance

between the transmitter and the microphone is 12 mm. The results are shown in Figure 5.19.

Figure 5.19 Frequency dependence of output sound pressure for a 2 mm $\times$ 2 mm pMUT element.

Figure 5.19 indicates that the output *SPL* reached its maximum at the resonant frequency. The output *SPL* is 107 dB at 41.2 kHz, much higher than that of the microspeaker prepared by thin piezoelectric film [72], which is 83.1 dB at 13.3 kHz.

The effect of the dc bias, the driving voltage and the measuring distance on the output *SPL* and resonant frequency of the transmitter is also investigated. Figure 5.20 shows the results. The output *SPL* increases with the increase of the applied dc bias and saturated at certain dc bias level of 30 V as shown in Figure 5.20(a) at which the polarization of the film approaches saturation. Figure 5.20(b) shows that the output *SPL*

increases with the driving voltage and decreases with the increase of the measuring distance.

Figure 5.20 Output SPL at resonance frequency versus (a) dc bias (ac driving voltage of 30 V_{p-p}), (b) peak-to-peak driving voltage (dc bias voltage of 30 V), and distance between measuring point and transmitter (bias 30 V, 30 V_{p-p}).

Not only does the output *SPL* increase with the dc bias, but the resonant frequency also shifts to a high value with increasing dc bias, as has been discussed in section 5.3.1. Figure 5.21 shows the result of a fabricated transmitter with a size of 1.5 mm by 1.5 mm and 3.5 mm thick PZT film. The resonant frequency shifts from 76 kHz to 76.7 kHz and the output sound pressure increases from about 5 Pa to 12 Pa as the dc bias increases from 15 V to 35 V.

Figure 5.21 Relation between dc bias and resonance frequency of a fabricated transmitter (with size of 1.5 mm $\times$ 1.5 mm) driven by 3.5- μ m-thick PZT film.

5.3.3 Directivity of emitting ultrasound beam

The directivity of the ultrasonic array is actually what we most concern about in beam forming and beam steering applications. In the measurement of directivity of

emitting ultrasound beam, the array is held in a holder for stable support and rotated by a rod attached to the holder. All the array elements is electrically connected in parallel and excited simultaneously by the same ac voltage source. An acousto-optic sensor with much improved bandwidth is set in symmetrical axes perpendicular to the plane of the array to detect the output ultrasound. The sensor possesses a diaphragm structure which can be driven to vibrate by the coming ultrasound beam. The displacement of the membrane vibration is then measured by an optical means. In this way, the measured membrane displacement is actually representing the intensity of ultrasound. The distance between the sensor and the array is 300 mm, where the far-field condition is satisfied. The displacement output of the acousto-optic sensor in response to the radiated ultrasound is utilized as the measure of sound pressure.

Figure 5.22 The directivity patterns of pMUT array on SOI wafer measured by the diaphragm type acousto-optic ultrasonic sensor.

The tested array consists of 37 elements with a size of 1.5 mm by 1.5 mm. It is soldered after being diced from the same SOI wafer as shown in Figure 5.11. An ac driving voltage of 10 V_{p-p} superimposed on a dc bias of 30 V is applied across the 6-μm-thick piezoelectric layer during measurement. The array is rotated from -90° to 90° with respect to the normal direction of the sensor. Each measurement is taken at every one degree. The radiation pattern of the array measured at resonant frequency of 163 kHz is shown in Figure 5.22. It can be seen from the figure that, the main lobe is very sharp and tall, which indicate a good directivity of the array transmitters. However, there are still some peaky side lobes at certain angles. This is considered due to the slight scattering in the piezoelectric displacement and the center resonant frequency of each element.

5.4 Summary and conclusions

In this chapter, new types of piezoelectric pMUT arrays for ultrasonic transmitter application are successfully developed based on the combination of silicon micromachining technology and hybrid PZT film deposition technology. Design issues and fabrication processes are discussed in details. Square or rectangular diaphragms with size ranging from 0.1 mm to 2 mm are fabricated. The elements are arranged to form different types of ring arrays and linear arrays. The performance of the prototype devices are investigated in terms of membrane deflection, emitting sound pressure, and directivity of emitting ultrasound beam. The resonant frequency dependence on the element size and the dc bias are discussed. High output *SPL* up to 110 dB and desirable directivity patterns are achieved.

CHAPTER SIX

CONCLUSION AND RECOMMENDATIONS

6.1 Conclusion

This thesis has aimed at the development of piezoelectric MEMS devices, or more specifically, the design and fabrication of diaphragm-type piezoelectric micromachined ultrasonic transducer (pMUT) arrays for directional ultrasound radiating applications. The entire work covers a wide variety of related issues, from material preparation and integration, instrumentation for material characterization and characterization methods, to prototype device design and fabrication. Major accomplishments of the thesis are listed below:

1. A study of sol-gel routes has been carried out to provide detailed information about the phase formation process during PZT thin film fabrication. PZT sols are prepared using lead acetate trihydrate, zirconium acetylacetonate, titanium isopropoxide, and acetylacetone as starting reagents, and acetic acid,

2-methoxyethanol, and 1,3-propanediol as solvent. Thermal analyses (DTA/TGA) are carried out for the samples, and Kissinger's method is employed to study the kinetics of phase formation and transition. It has been found that three kinds of reactions, pyrochlore crystallization, de-oxygen, and perovskite crystallization, make up the whole process of perovskite formation. The effective activation energies of each reaction are calculated as 52.6, 246.7, 74.2 kJ/mol for acetic acid gel, and 457.2, 68.1 kJ/mol for MOE gel. Acetic acid has an advantage over MOE as solvent, for its low activation energy required for phase transition.

2. PZT (53/47) films with thickness ranging from 0.5~1.1 μm are fabricated using acetic acid sol-gel method on silicon substrate. By employing modified acetic acid based PZT sol, uniform, dense films with a single layer thickness up to 0.4 μm have been achieved. This process enables several-micron-thick PZT films being fabricated only by less than 10 steps of coating. Macro-scale cracks are avoided by introducing a pre-annealing step. Being finally annealed at 650°C for 30 min, the films show single phase of perovskite, and exhibit good ferroelectric properties. The remanent polarizations P_r and coercive field E_c are measured as 15.5 $\mu\text{C}/\text{cm}^2$ and 31.5 kV/cm for a typical 1.1- μm -thick PZT thin film sample.
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. By suspending PZT powder in PZT xerogel solution,

uniform and stable slurry has been made, which 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 milling and loading of powder has been observed. The grains in the film develop 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.

4. In the development of a high-sensitivity interferometric method for piezoelectric characterization, a modulation technique has been proposed and realized to overcome the random drift problem of the fringes caused by the environment or even the intensity variation of the laser source. An ultrahigh out-of-plane displacement resolution down to picometer required for piezoelectric characterization of thin films has been achieved.
5. A novel scanning homodyne interferometer has been developed based on the combination of a modulated Mach-Zehnder interferometer and a high-precision 2-dimensional translation stage. Due to its ultrahigh out-of-plane resolution (down to picometers) and wide bandwidth potential, the scanning interferometer is well suited for characterization of piezoelectric thin films as well as for vibration measurement of MEMS devices.

6. Various PZT thin/thick film samples prepared with different processing parameters have been characterized using the newly developed scanning Mach-Zehnder interferometer. It is demonstrated that the apparent longitudinal piezoelectric displacement of the film samples can be easily identified and measured by fine scanning across the top electrode. The apparent longitudinal piezoelectric coefficients at different dc bias voltages are measured for various film samples. It is found that CIP treatment shows favorable effect on the piezoelectric properties of the PZT hybrid thick films and that the concentration of the sol-gel solutions is not an influential factor. As the data obtained comprise information of both longitudinal and transverse piezoelectric properties, it's feasible to use the line-scan data with the aid of a proper analytical model or finite element model to work out the transverse properties or the mechanical properties of the piezoelectric films.
7. New types of piezoelectric pMUT arrays for ultrasonic transmitter application have been successfully developed based on the combination of silicon micromachining technology and hybrid PZT film deposition technology. Design issues and fabrication processing have been discussed in details. Various configurations of ring arrays and linear arrays have been fabricated with square or rectangular diaphragm element size ranging from 0.1 mm to 2 mm. The performance of the prototype devices has been investigated in terms of membrane deflection, emitting sound pressure, and directivity of emitting ultrasound beam. The resonant frequency dependence on the element size and

the dc bias has been found well consistent with the clamped-plate model.

Ultrasound beam with high output *SPL* up to 110 dB and desirable directivity patterns has been achieved.

6.2 Recommendations

With regard to the characterization of piezoelectric properties of thin/thick films, the apparent longitudinal piezoelectric coefficient of PZT films has been measured by a scanning interferometric method. However, the transverse piezoelectric coefficient has not been investigated. By using the scanning interferometric method, the displacement and the curvature of the substrate bending deformation can be accurately determined. These data are closely related to the transverse piezoelectric coefficient (d_{31}) of the films as well as the mechanical properties of both the piezo films and the substrate. As the Young's modulus and Poisson's ratio of the silicon substrate are available, it is recommend that a proper analytical model or finite element model should be established in order to calculate the transverse properties or the mechanical properties of the piezoelectric films based on the measured substrate bending deformation. These properties will be quite essential for either material research or piezoelectric MEMS device design.

In addition, it should be pointed out that we have assumed the deformation of the substrate outside the electrode region to be the same as that below the top electrode.

Chapter VI Conclusion and recommendations

According to the results of our FEM analysis [66], this assumption is only valid when the size of the top electrode exceeds a critical value (around 1 mm). As the electrode dimension of our samples is 0.8 mm, this assumption would not cause an error above 5%. The FEM analysis reveals that the measured apparent d_{33} is strongly dependent on the electrode size when the size is below the critical value. It is recommended that an experiment, i.e., the measurement of the apparent d_{33} for a series of different electrode sizes, be carried out in order to verify the FEM analysis results.

In Chapter 5, we didn't explore the sensing abilities of the piezoelectric transducers. Theoretical analyses and experiment results [92] have revealed that, for the diaphragm-type pMUTs being used as ultrasound sensors, the received signal will be in the range of micro volts. However, our current experimental setup is not able to single out the weak signal from the electrical noises. In the future, ultimate design of the pMUT arrays for medical imaging applications shall include the integration of preamplification electronics with the pMUTs into one chip. As the preamplified signal can readily be detected, the pMUT arrays will be able to serve both as emitters and as sensors for the application of pulse-echo mode ultrasonic imaging.

AUTHOR'S PUBLICATIONS:

Journal papers

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