A new PZT piezoelectric sensor for gravimetric applications using the resonance-frequency detection

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\textbf{A R T I C L E  I N F O}

Article history:
Received 10 March 2008
Received in revised form 15 March 2009
Accepted 20 March 2009
Available online 31 March 2009

Keywords:
Lead zirconate titanate (PZT)
Piezoelectric
Biosensor
Resonance frequency

\textbf{A B S T R A C T}

Piezoelectric sensors made of quartz, Pb(Zr,Ti)O\textsubscript{3}, Pb(La,Zr,Ti)O\textsubscript{3}, or Pb(Zr,Ti,Sn)O\textsubscript{3} have rapidly been developed recently because of the potential applications in devices such as biosensors, accelerometers, pressure sensors, and ultrasonic transducers. However, the development of devices with reduced size but with improved sensitivity is highly important. With this idea, the study aims to develop a lead zirconate titanate (PZT) chip as a novel gravimetric biosensor using the resonance feature in biomolecule detection. The PZT thin film characterized by the X-ray diffractometer (XRD) has a perovskite structure. The fabricated PZT sensor was designed with 250 μm × 250 μm-sensing areas of electrodes, determined by the measured impedance at 98.5 MHz frequency. The morphology and cross-section of scanning electron microscope (SEM) images show that the thickness of the spin-on PZT layer was about 50 nm and the crystal grain size was less than 50 nm. Moreover, an evaluation circuit consisted of a resonance circuit and a frequency-to-voltage circuit was established to detect bovine serum albumin (BSA) protein. The PZT sensor, combined with evaluation circuit, showed a high sensitivity of 62.8 Hz cm\textsuperscript{2}/ng. The detection sensitivity was enhanced by 300 folds than that of traditional quartz crystal microbalance (QCM).

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1. Introduction

The piezoelectric device was the earliest commercial application of microfabrication technology in many products. The device was widely used in motorized, biomedical, industrial measurement, automatic control, and other electronic products. This device composed of microelectronics and piezoelectric actuators with the advantage of being energy-savers and ideal solutions to small or portable products.

Recently, however, the sensitivity of piezoelectric sensor has been questioned as it has gained increased popularity. Among its different kinds, the quartz crystal microbalance (QCM), was the first piezoelectric sensor developed and used to detect biomolecules [1].

The QCM, which uses the resonance enhancement of mass sensitivity through vibration of piezoelectric device at the quartz crystal resonance-frequency level, is a powerful operating method for biosensors. The resonant frequency resulting in vertical waves travels to the sensor surface, so their maximum frequency was limited because of the minimum obtainable quartz thickness. Therefore, the frequency of the vertical wave is related to crystal thickness and also has been directly related to their sensitivity. The resonant frequency refers to the type of dependence that Sauerbrey [2] claimed to exist in a relationship between variables needed to determine the mass changes in thin films. The findings are summarized in the following formula:

\[ 0 < \frac{\Delta f}{A K_f} = \frac{2 \Delta \omega^{-2}}{A \sqrt{\rho \mu}} \Delta m = k f_0^2 \Delta m. \]

In the equation, \( f_0 \) is the resonant frequency of fundamental mode, \( \rho \) and \( \mu \) are the density and shear modulus, respectively, of the piezoelectric materials, \( A \) is the area of resonance, \( \Delta f \) is the change of the frequency, and \( \Delta m \) is the change of mass deposited on the surface of the sensor electrode, \( K \) is a constant. According to Sauerbrey’s equation, the square of resonant frequency \( (f_0^2) \) was inversely proportional to \( \Delta m \). However, the definition of sensitivity is related to the change of the resonant frequency, while it had proportioned to the change in mass for per square centimeter, according to the expected relationship:

\[ \text{Sensitivity} = \frac{\Delta f}{\Delta m/A}. \]

Thus, developing a high-frequency resonator could measure the change of the slightest mass and improved the detection limited simultaneously.
Piezoelectric materials have been rapidly developed in recent years mainly due to their potential of being used as critical devices. This material has two unique properties which are interrelated. The first is the piezoelectric effect used in sensing applications, such as in force or displacement sensors. Another is the inverse piezoelectric effect used in actuation applications, such as in motors and devices that precisely control positioning. The inverse piezoelectric effect is also used in generating sonic and ultrasonic signals [3,4].

The development of micro-electromechanical systems (MEMS) has also supported new potential applications of thin layers in micropositioning, among them, was the lead zirconate titanate (PZT) material, which was widely used because of their large electromechanical coupling coefficients, temperature stability and high resistance to depolarization from mechanical stress and high-driving voltages. Several techniques in creating PZT thin films under the perovskite phase have been undertaken to improve their ferroelectric property [5]. Moreover, magnetron sputtering, electron beam evaporation and pulsed laser ablation, solution-based deposition route for sol–gel process have been gaining popularity as they allow convenient tailoring of composition and microstructure of the thin film.

This paper studied the behavior of PZT device using the frequency modulation (FM) detection method as an innovative high-frequency sensing device. Because of their large piezoelectric coefficients, lead zirconate titanate (PZT) thin films are among the best materials for use in ultrasonic transducers. However, the researchers have shown how the FM detection system and the PZT sensor could be used by activating gravimetric detection through frequency shift. The advantage of the the FM detection method could be distinguished easily through frequency shift, and the applied gravimetric on the PZT chip surface could be observed precisely. The researchers expected high-resolution type gravimetric sensing through the FM detection method for micro-gravimetric sensor in various environments. Furthermore, the study showed the potential of the piezoelectric thin film as a microfabrication sensor, which could be applied in highly sensitive detection processes. Finally, the study found that the PZT ceramic elements of the piezoelectric device produced a small displacement with high force capability when voltage was applied.

2. Research methodology

2.1. Preparation of piezoelectric chip

The researchers applied the planar square element. The top electrode of the experiment was 250 μm × 250 μm, and the piezoelectric layer was enclosed between two metal electrodes in a metal/ferroelectric/metal (MFM) structure (see Fig. 1). The film was prepared using sol–gel method on commercial PZT materials. The fabrication of the PZT chip was used in thin film micro–machining technology. The researchers used commercially available silicon wafer and coated SiO₂ layer (680 Å) by thermal oxidation to be a substrate for the process. The bottom electrode layer of Ti/Pt was deposited using a thermal evaporator. The thickness of Ti/Pt was measured at 50/100 nm. The PZT layer was coated by sol–gel method. Sol–gel PZT (52/48) solution was procured from Kojundo Chemical Lab. Corp., Japan. The PZT sol–gel deposits on the substrate were spin-coated at 3000 rpm/min for 30 s. After each coating, the film was dried at 180 °C for 5 min to remove the residual organic species. Then, the film was pyrolized at 350 °C for 5 min to remove the residual organic species. The thin film was wet-etched using the buffered oxide etchant (BOE) through a microlithographic process. Finally, crystallization was achieved by annealing at 700 °C in air. The PZT thin film consisted of 15 coating layers, the thickness measured approximately at 50 nm. The top electrode of Cr/Au was prepared using a thermal evaporator on the PZT surface. The thickness of top electrode was measured at 50/100 nm. The overall thickness was determined by surface profilometer.

2.2. Characterization of piezoelectric layers

The morphology of PZT layer was characterized by scanning electron microscope (SEM). The scanning was done to obtain grain size and thickness. The composition of crystallization structure was determined by X-ray diffraction system (XRD). The XRD patterns were recorded through a Bruker thin film diffractometer (D8 Advanced). The fundamental electrical properties were evaluated using I–V measurements. To obtain the hysteresis data, the ferroelectric property from the movement of domain walls was analyzed by ferroelectric system (TF 2000, Aixacct), and the leakage current analysis was measured with Kethley 4200. The study also used the HP E8361A network analyzer to observe the relationship between impedance and phase. Through the characteristic of impedance and phase, the researchers observed the resonant frequency of the piezoelectric chip [6].

2.3. Detection system fabrication

This study used the Colpitts oscillator circuit to enhance the PZT resonance intensity and develop the oscillating circuit in the detection system (the oscillator was an unconditional stable amplifier with a signal feedback). The resonance frequency was characterized using the oscillating circuit by frequency to the voltage converter, which includes a frequency modulation circuit and a local oscillator circuit. The high–resolution capacity of the PZT chip was detected in an ambient condition through mass load and frequency modulation (FM) detection method [7].

The resonance frequency of mass detection on PZT chip was measured through the output voltage change in the detection system. The measurement system included the frequency readout circuits, one data acquisition card (PCI-6052) and analysis software (Labview 8.2). The data acquisition card and analysis software were purchased from the National Instruments Corporation, an institution that improved the analogical signal converter to a digital signal, and real-time monitoring via programmed software (Labview 8.2). The output signal (DC level) of the PZT piezoelectric chip was amplified using an internal amplifier circuit of the frequency demodulation circuit; it generated a high voltage difference from the gravimetric variations on the chip. The customized Labview software was developed to identify and decode individual mass...
loading of the acquired detection signal through data acquisition system (Fig. 2).

3. Results and discussion

3.1. Properties of PZT thin film

The cross-section and surface morphology of the PZT piezoelectric films was shown in Fig. 3 by the SEM micrographs. The film showed grain and void-free structures of less than 50 nm. The thickness of the film by 15 cycles of drying/sintering was about 500 nm and all films were crack-free. From the XRD results, the researchers found that the bottom electrode of Pt proved to have a good orientation peak of (1 1 1) [8]. The PZT film deposited on Pt (1 1 1) grew preferentially along the (1 1 1) orientation. The microstructure of Pt and PZT thin films varied with the combination of the final heat-treated conditions and preparation process. Likewise, the patterns of PZT films showed the diffraction peaks of (1 0 0), (1 1 0), (1 1 1), (2 0 0) and (2 1 1) crystal planes found (see Fig. 4). Based on the previous reports [9,10], the PZT thin film had poly-crystal lattices near morphotropic phase boundary (MPB) and showed higher dielectric constant, piezoelectric constant and electromechanical coupling factor. Because of the PZT near the morphotropic phase boundary (MPB) composition, the film with a mixed texture of [1 1 1] and [1 0 0] had a high dielectric constant due to the PZT having multiple polarization directions of these lattices [11].

3.2. Leakage current analysis

The noticeable decrease in I–V was found to have resulted from the change in the conductive nature of the electrode transmission measurement. Based on previous studies [12,13], increasing the thickness of PZT thin film could decrease the leakage current because the thick film is tighter than a thin film. Therefore, the proposed PZT film was coated 15 cycles using a spin-coating process to decrease the leakage current. The leakage current density levels applied voltage ranging from 0 to 5 V was below $2 \times 10^{-6}$ A/cm$^2$ [14]. These results showed that the current transported through the PZT material resulted from the electric field and enhanced the schottkey emission. The sample showed the trapped free space-charge-limited current.

3.3. Ferroelectric hysteresis properties

Based on the ferroelectric property, the correlation between the strains and the electric field was due to the normal converse piezoelectric effect and the switching of domain walls. The ferroelectric property of PZT film was evaluated at room temperature, at 100 Hz by TF 2000 system (Aixacct Co.). Fig. 5 shows the polarization–electric (P–E) field hysteresis loop of a 500 nm thin PZT film on Pt/Ti/SiO$_2$/Si with an upper electrode. The remnant polarization (Pr) and coercive field (Ec) values determined from P–E hysteresis loop were 6.12 μC cm$^{-2}$ and 59.19 kV cm$^{-1}$. The polarization curves of the PZT thin film applied in the electric field loop showed a good square shape. The researchers observed slightly lower Pr and Ec in comparison with present reports [15]. This showed that the PZT material on the resonant sensor acted well as an active layer to generate the high actuating force. The result showed that the PZT film had a good ferroelectric property.
3.4. Detection system characterization

The resonance was obtained by a network analyzer [16]. The resonance frequency occurred at the reactive component of the impedance phase, which was zero. Thus, Re(Y) was at the maximum level [17]. Frequency sweeps covered a range of 30 MHz around the resonance with a 200-point resolution. A resonance chip has two frequencies of zero phases. The series resonance occurs at the first frequency. At this point, the PZT piezoelectric chip appears resistive in the circuit, impedance is at a minimum and current flow is maximum. As the frequency is increased beyond the point of series resonance, the PZT piezoelectric chip appears inductive in the circuit. When the reactance of the motional inductance and shunt capacitance cancel, the PZT piezoelectric chip is at this point, impedance is maximized and current flow is minimized. The resonant points of a ceramic resonator are basically defined as the maximum and minimum impedance at the phase of 0°. Therefore, the resonance frequency about 98.5 MHz of the PZT chip was obtained by impedance and phase, as shown in Fig. 6.

Following the identification of the PZT resonance frequency, this study showed that the Colpitts oscillator circuit drove the observed vibration in the PZT device. When the resonator worked, the sine wave across the PZT chip was amplified by a transistor circuit, which it used as a signal converter circuit from frequency (V_PZT) to DC level (V_DC) to determine the frequency change effectively (see Fig. 7). The sensing system includes the PZT chip, readout circuits, one data acquisition card and software (Labview 8.2). Therefore, the PZT resonance signals could be received with this system, which also simplifies the monitoring of its sensing characteristics (see Fig. 8(a)). The base potential of sensor was approximated to 0 V. Moreover, the mass sensitivities of the PZT chip were detected by the dropping water (10 μl). When the water dropped in the chip surface, the resonance frequency and DC level reduced in the sensing system considerably. The time of signal response was less than 3 s. After 30 min, the output voltage was increased and determined by the monitor. The results showed that the increase in the PZT resonance frequency because of the evaporation of residual water (see

![Fig. 5. Polarization electric (P-E) field hysteresis loop of the PZT chip.](image)

![Fig. 6. PZT resonator frequency characteristic.](image)

![Fig. 7. Schematic diagram of the resonance-frequency detection circuit.](image)

![Fig. 8. Characteristic of the resonance-frequency variation from the detection system (a) the hardware of the measurement system and (b) the signal was connected to the monitor.](image)
reaching 62.8 Hz cm² ng

can be observed then that the sensitivities were noticeably high,

study presented that novel PZT sensor system has great potential

magnitude higher than the 10 MHz quartz crystal microbalances. This

applies to biomolecule mass detection was about 300 folds of mag-

change of the molecule. We also proved the PZT sensor system

can adjust the base voltage to increase its accuracy. This novel

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