(Short Communication)

# The Fabrication and Characterization of PZT Thin Film Acoustic Devices for Application in Underwater Robotic Systems

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#### ABSTRACT

A high frequency spectrum lead zirconate titanate (PZT) thin film acoustic device was fabricated and studied for application using an underwater technique. The radio frequency (RF) planar magnetron sputtering method was used to deposit PZT thin film. The deposited PZT thin film IC (integrated circuits) fabrication processes were used to fabricate the acoustic devices. The optimized annealing conditions were 650°C and 20 min for PZT thin film deposited at 350°C for 2 h. The obtained PZT thin film had a dielectric constant of 869, a free dielectric constant  $\varepsilon_{33}^T$  of about 893, a dielectric loss of 0.3, a concorcive electric field of 0.061 KV/cm, a piezoelectric constant  $d_{33}$  of 2.03 pm/V, a piezoelectric constant  $g_{33} = d_{33}/\varepsilon_{33}^T$  of 2.57 × 10<sup>-4</sup> vm/N and a polarization level of 112.5 nC/cm. The fabricated PZT thin film acoustic devices can be used as transmitters on receivers. The highest levels of transmission sensitivity and receiving sensitivity, which can be obtained, are 76 dB and -75 dB, respectively. The acoustic device has better performance when poled PZT thin film is used.

Key Words: PZT thin film, acoustic devices, underwater technique

# I. Introduction

Piezoelectricity was first discovered by Jacques and Pierre Curie in 1880, and other materials later discovered included reochelle salt (NaKC<sub>2</sub>H<sub>4</sub>O<sub>6</sub>·4H<sub>2</sub>O), barium titanate (BaTiO<sub>3</sub>), lead titanate (PbTiO<sub>3</sub>) lead zirconate titanate (PbZr<sub>0.52</sub>Ti<sub>0.48</sub>O<sub>3</sub>), zinc oxide (ZnO), aluminum nitride (AlN), polyvinyliden fluoride (PVDF) etc. Since lead zirconate titanate (PZT) has excellent piezoelectric properties, a high Curies temperature, high spontaneous polarization and high electromechanical coupling coefficient, it has become an important industrial product.

There are many applications of PZT ferroelectric materials, including the measurement of object distance underwater. For underwater techniques, ultrasonic acoustic sensors have better characteristics than do optical devices. Since ultrasonic waves can transmit the through all materials thought not in a vacuum, they are the best choose for application in the detection of opaque objects, underwater image techniques, and in non-destructive measurement.

PZT is the main material used to fabricate commercial acoustic devices. For PZT distance measuring sensors, such as RPS8000 (Migatron, U.S.A.), operating at a frequency of 300 KHz, the response is linear as shown in Fig. 1. The measurement technique is easy to perform, and the measurement results are accurate. However, using the same sensors to measure distance underwater, the error in distance measurement is seriously enhanced. Figure 2 shows the relationship between the voltage and distance in distance measurement underwater. The linearity of the measured data is poor. In addition, the l range of short distance measurement is limited. Therefore, the operating frequency must be increased, and the device structure should be improved to measure distances accurately. Furthermore, to compete with commercial optical cameras in measuring distances, the measuring distance resolution of acoustic devices must be enhanced. The major im-



Fig. 1. The relationship between the ultrasonic sensor output and object distance. It is linear from 10 cm to 30 cm.

provement is made to use high operating frequencies. Devices should be developed for all distance ranges, including long and short distance measurement. On the other hand, a thin film device is a better choice than a bulk piezeoelectric ceramic sensor for high frequency acoustic devices. In addition, the thin film acoustic devices fabrication is similar to fabrication process of integrated circuits (IC) process, which will be reduce the fabrication cost of these devices. On the other hand, there are different techniques have been adopted for the deposition of PZT films, which include electron beam evaporation (Oikawa and Toda, 1976), Rf diode sputtering (Okada, 1977, 1978), ion beam deposition (Pignoleta and Levy, 1990; Castellano and Feinstein, 1979), RF planar magnetron sputtering (Krupanidhi et al., 1983; Takayama and Tomita, 1989; Sakashita and Segawa, 1993), MOCVD (Choi and Kim, 1993; Braun et al., 1993; Larsen et al., 1994; Peng and Desu, 1992; Kaub et al., 1994) ECR (Auciello, 1993), laser ablation (Frantti and Lantto, 1994; Horwitz et al., 1991; Safari and Pfeffer, 1992; Leuchtner et al., 1992; Yi et al., 1988), and sol-gel (Sanchez et al., 1990; Dey et al., 1988; Amanuma et al., 1993; Udayakumar et al., 1995; Kwok and Seshu, 1993). PZT thin films were deposited using an RF planar magnetron sputtering system in this experiment. The advantages of RF planar magnetron sputtering are low temperature, low loss and ease of to control. In this experiment, RF planar magnetron sputtering was used to deposite PZT thin film for Pt/PZT/Pt/SiO<sub>2</sub> acoustic devices.

### II. Fabrication and Analysis of PZT Thin Film

In general, the deposited PZT film has a near amor-

phous structure, which after high temperature annealing processes are applied it can change to a polycrystalline structure (Sakashita and Segawa, 1993). In this experiment, the phase changes were observed using by X-ray diffraction (XRD) (Siemes, German). In addition, the surface morphology of the PZT film was obtained by means of scanning electron microscopy (SEM) (Hitachi, Japan).

The process PZT used to fabricate thin film was as followed. After the surface of the n-type (100) silicon is cleaned, a 0.25  $\mu$ m oxide layer was produced using a wet oxidation process. Then, a 0.3  $\mu$ m Pt electrode on the oxide layer was evaporated. Finally, the PZT thin film was deposited at 350°C for 2 hours. After the PZT thin film was deposited, an annealing process was needed. The annealing temperature of the sample was 650°C, and the annealing time was 20 minutes; then the sample was cooled to room temperature. Annealing temperature which are too high or low are disadvantages for PZT thin film, since too low annealing temperature is difficult to transform the amorphous structure into a polycrystalline structure when the temperature is too low, and because high Pt thermal stress will cause the PZT thin film to crack when the annealing temperature is higher than 700°C. Furthermore, if the annealing temperature is higher than 800°C, the PbO will be volatilized from PZT thin film that will produce worse quality of PZT thin film. In this experiment, the annealing temperature for the fabrication of acoustic devices was 650°C. If the PZT thin film was annealed for 5 minutes, its structure still had some perovskite phase and some pyrochlore phase. When the annealing time was increased to 10 minutes, the thin film appears all perovskite structure. As indicated in Fig. 3, the X-ray diffraction count of (110) unclear decreased



Fig. 2. The relationship between the ultrasonic sensor output and object distance under water.



Fig. 3. XRD patterns with different annealing times (Pt substrate, deposition temperature 350°C, R.F. power 100 W, Ar = 10 SCCM, deposition time 2 hr, annealing temperature 650°C.)

when the annealing time was longer than 40 minutes because the quality of the perovskite structure became worse owing to the overvolatilization of PbO. Figure 4 shows the SEM patterns of deposited PZT thin film surfaces which were deposited at 350°C and then annealed at 650°C for 20 minutes. The grain size of the PZT thin film deposited under the above conditions was about 130 nm. Figure 5 shows the SEM patterns of PZT thin film surfaces which were deposited at 350°C and annealed at 850°C for 5 minutes. The grain size increased with the increase of the annealing temperature, but an annealing temperature which was too high caused the PZT thin film to crack. Very high annealing temperatures were not suit-



Fig. 4. The surface morphology of PZT thin films annealed at 650°C for 20 min. and 5 min. rapid temperature annealing.



Fig. 5. Cracks produced during higher temperature annealing.

able.

In this experiment, the optimum annealing time was 20 minutes at an annealing temperature of 650°C. The sandwich structure Pt-PZT-Pt was used in this study to measure the ferroelectric properties of the PZT thin film, which are shown in Fig 6. An HP4192 low frequency impedance analyzer was used to measure the dielectric constant and dielectric loss, and the measuring frequency was fixed at 1 KHz. The measurement results were as follows: a dielectric constant of about 869, a free dielectric constant  $\varepsilon_{33}^{T} = 893$  and a dielectric loss of about 0.3. In addition, the P-E hysteresis loop was measured using the modified Sawyer-Tower circuit. Figure 7 shows the measured results: the coercive field was about 0.061 kv/cm, and the polarization level was 112.5 nc/cm. In addition, the piezoelectric constant  $d_{33}$  was 2.03 pm/V, and the piezoelectric constant  $g_{33} = d_{33}/\varepsilon_{33}^T$  was 2.57 × 10<sup>-4</sup> vm/N.

# III. Fabrication of PZT thin film Ultrasonic Sensor

The process used to fabricate the PZT thin film acoustic sensors were as follows. First, a lithography technique was used to form a window on the back of the silicon substrate. Then, buffer-HF was used to etch the oxide layer and stripping resist. The window on the back of the



Fig. 6. The sandwich structure of the PZT thin film ultrasonic sensors.



Fig. 7. The hysteresis loop of the PZT thin film.

silicon substrate was etched to form a  $100-\mu m$  diaphragm using KOH solution. Then, Pt/PZT/Pt films were deposited, respectively. After the bottom and top electrodes were bonded separately, the PZT thin film was poled under an electric field of 10 kV/cm at a temperature of 130°C. Finally, the sample was packaged using BNC (baby N connecter), silicon gel and a tube of teflon after electrical testing was conducted to form an acoustic device. Then, the characteristics of the PZT thin film acoustic sensor were measured. The sensitivity of the sensor was measured based on the reciprocity principle in a water tank (Chang and Chen, 1997). A B&K 8104 hydrophone (Bruel Kjaér, Denmark) was the reference source. When the transmission sensitivity was measured, the hydrophone acted as a receiver. On the other hand, when the receiving sensitivity was measured, it acted as a transmission source. The PZT thin film acoustic sensor was driven using an HP8166A pulse generator (Hewlett Packard, U.K.). Its driving voltage was fixed at 10 Vp-p, and its operation frequency range was from 100 KHz to 4 MHz. The frequency spectrum was analyzed using an HP4195 network analyzer (Hewlett Pakard, Japan). All the operation processes were carried out in a water tank, whose height, length and width were 2.1, 1.8 and 1.5 meters, respectively. Figure 8 shows the measured results of the transmission response, where the PZT thin film fabricated in the experiment served as a transmitter and a B&K 8104 hydrophone served as a receiver. From Fig. 8, it can be seen that the transmission sensitivity of the poled PZT thin film sensor was better than that of the unpoled PZT thin film sensor when the frequency was above 1 MHz. The poled PZT thin film sensor had better characteristics because the poled PZT thin film had better piezeoelectric properties. The receiving sensitivity of the PZT thin film sensors is shown in Fig. 9. From Fig. 9, it can be seen that the receiving sensitivity of the poled PZT thin film sensor was better than that of the unpoled PZT thin film sensor. It can be seen that the receiving sensitivity was in a high



Fig. 8. The transmission sensitivity of the PZT thin film ultrasonic sensors.



Fig. 9. The receiving sensitivity of the PZT thin film ultrasonic sensors.

frequency range, and that the result matches the transmission measurement result. The highest level of receiving sensitivity was –75 dB at 4 MHz. Therefore, the PZT thin film sensors fabricated in the experiment were suitable for operation at high frequencies. The fabricated devices exhibited high sensitivity at higher frequencies because the deposited PZT thin film had a higher electric resonant frequency. In addition, the field pattern of the fabricated devices was measured based on the distribution of the acoustic field. The results are shown in Fig. 10, which shows that the field response was uniform for the PZT thin film sensors fabricated in this experiment. The poled devices and unpoled devices had similar results apart from the finding that the poled devices had higher levels of sen-

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Fig. 10. The acoustic field of the PZT thin film sensors: (a) poled (b) unpoled.

#### sitivity.

## **IV. Conclusion**

A PZT thin film acoustic device was fabricated and studied in this experiment using an underwater technique. A Pt/PZT/Pt/SiO2/Si structure was used to fabricate the acoustic devices. The PZT thin film was deposited using RF planar magnetron sputtering. The characteristics of the deposited PZT thin film were also analyzed. The deposited PZT thin film was annealed at 650°C for 20 minutes to form a perovskite structure, which enhanced the piezoelectric properties of the deposited thin film and improved the characteristics of the fabricated acoustic device. In addition, the poling PZT thin film technique employed was also effective in improving the characteristics of the fabricated acoustic device. The optimized properties of the PZT thin film in this experiments were a dielectric constant of about 869, a free dielectric constant  $\varepsilon_{33}^{T} = 893$ , a dielectric constant of about 0.3, a polarization level of about 112.5 nC/cm, a coercive field of about 0.061 kV/cm, a  $d_{33}$  of 2.03 pm/V and a  $g_{33}$  of 2.57  $\times 10^{-4}$ vm/N. The optimized PZT thin film was also used to successfully fabricate an acoustic device. The device could be used as a transmitter or as a receiver. The sensitivity of the device was measured using the reciprocity method under water. The highest transmission sensitivity was 76 dB at 4 MHz, and the receiving sensitivity was 75 dB at 4 MHz. The acoustic device had better transmission and receiving sensitivity when poled PZT thin film was used. Furthermore, the measurement results show that in a higher frequency range, both the transmission and receiving sensitivity were higher. The fabricated acoustic devices can be used as high operating frequency range devices in underwater applications.

#### References

Amanuma, K., T. Hase, and Y. Miyasaka (1993) Crystallization behavior

of Sol-Gel derived  $Pb(Zr,Ti)O_3$  thin films and the polarization switching effect on film microstructure. *Appl. Phys. Lett.*, **65**(24), 3140-3142.

- Auciello, O. (1993) Synthesis and characterization of  $Pb(Zr_xTi_{1,x})O_3$  thin films produced by an automated laser ablation deposition technique. *J. Appl. Phys.*, **73**(10), 5197-5207.
- Braun, B., S. Kwak, and A. Erbil (1993) Exitaxial lead zirconate-titanate thin films on sapphire. *Appl. Phys. Lett.*, **63**(4), 467-469.
- Castellano, N. and L. G. Feinstein (1979) Ion-beam deposition of thin films of ferroelectric lead zirconate titanate (PZT). J. Appl. Phys., 50(6), 4406-4411.
- Chang, C. C. and Y. E. Chen (1997) The fabrication of high sensitivity ZnO thin film ultrasonic devices through electrochemical etching technique. *IEEE Trans. on Ultrasonic, Ferroelectric and Frequency Control*, 44(3), 624-628.
- Choi, J. H. and H. G. Kim (1993) Deposition behavior of  $Pb(Zr_xTi_{1-x})O_3$ thin films by metalorganic chemical vapor deposition. *J. Appl. Phys.*, **74**(10), 6413-6417.
- Dey, K., K. D. Budd, and D. A. Payne (1988) Thin-film ferroelectrics of PZT by Sol-Gel processing. *IEEE Trans. Ultrason. Ferroelectr. Freq. Contr.*, 35(1), 80-81.
- Frantti, K. and V. Lantto (1994) Characterization of Pb<sub>0.97</sub>Nd<sub>0.02</sub> (Zr<sub>0.55</sub>Ti<sub>0.45</sub>)O<sub>3</sub> thin films prepared by pulsed laser ablation *J. Appl. Phys.*, **76**(4), 2139-2143.
- Horwitz, S., K. S. Grabowski, D. B. Chrisey, and R. E. Leuchtner (1991) In situ deposition of epitaxial Pb(Zr<sub>x</sub>Ti<sub>1-x</sub>)O<sub>3</sub> thin films by pulsed laser deposition. Appl. Phys. Lett., **59**(13), 1565-1567.
- Kaub, T. R., E. Takata, K. Tanaka, and K. Ohwada (1994) Characterirzation of piezoelectric properties of PZT thin films deposited on Si by ECR sputtering. *Sensors and Actuators A*, 45, 125-129.
- Krupanidhi, B., N. Maffei, M. Sayer, and K. El-Assl (1983) RF planar magnetron sputtering and characterization of ferroelectric Pb(Zr, Ti)O<sub>3</sub> films. J. Appl. Phys., 54(11), 6601-6609.
- Kwok, C. K. and B. D. Seshu (1993) Low temperature perovkite formation of lead zirconate titanate thin films by a seeding process. J. Mater. Res., 8(2), 339-343.
- Larsen, K. J., G. J. M. Dormans, D. J. Taylor, and P. J. van Veldhoven (1994) Ferroelectric properties and fatigue of PbZr<sub>0.51</sub>Ti<sub>0.49</sub>O<sub>3</sub> thin films of varying thickness blocking layer model. *J. Appl. Phys.*, **76**(4), 2405-2413.
- Leuchtner, E., K. S. Grabowski, D. B. Chrisey, and J. S. Horwitz (1992) Anion-assisted pulsed laser deposition of lead zirconate titanate films. *Appl. Phys. Lett.*, **60**(10), 1193-1195.
- Oikawa, M. and K. Toda (1976) Preparation of Pb(Zr,Ti)O<sub>3</sub> thin films by an electron beam evaporation technique. *Appl. Phys. Lett.*, **29**(8), 491-492.
- Okada, A. (1977) Some electrical and optical properties of ferroelectric lead-zirconate-lead-titanate thin films. J. of Appl. Phys., 48(7), 2905-2909.
- Okada, A. (1978) Electrical properties of lead-zirconate-lead-titanate ferroelectric thin films and their composition analysis by auger electron spectroscopy. J. Appl. Phys., 49(8), 4495-4499.
- Peng, C. H. and S. B. Desu (1992) low-temperature metalorganic chemical vapor deposition of perovskite  $Pb(Zr_xTi_{1-x})O_3$  thin films. *Appl. Phys. Lett.*, **61**(1), 16-18.
- Pignolet, W. A. and F. Levy (1990) Properties of  $Pb(Zr_xTi_{1-x})O_3$  thin films prepared by RF magnetron sputtering and heat treatment. *Mat. Res. Bull.*, **25**, 1495-1501.
- Safari, L. A. and R. L. Pfeffer (1992) Growth of epitaxial Pb(Zr,Ti)O<sub>3</sub> films by pulsed laser deposition. *Appl. Phys. Lett.*, **61**(4), 1643-1645.
- Sakashita, Y. and H. Segawa (1993) Dependence of electrical properties on film thickness in Pb(Zr<sub>x</sub>Ti<sub>1-x</sub>)O<sub>3</sub> thin films produced by metalorganic chemical vapor deposition. J. Appl. Phys., **73**(11), 7857-7863.
- Sanchez, L. E., S. Y. Wu, and I. K. Nailk (1990) Observation of ferroelectric polarization reversal in Sol-Gel processed very thin lead-zirconate-titanate films. *Appl. Phys. Lett.*, 56(24), 2399-2401.
- Takayama, R. and Y. Tomita (1989) Preparation of epitaxial Pb( $Zr_xTi_{1-x}$ ) O<sub>3</sub> thin films and their crystallographic, pyroelectric, and ferroelec-

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tric properties. J. Appl. Phys., 65(4), 1666-1670.
Udayakumar, R. P., J. Schuele, J. Chen, S. B. Krupanidhi, and L. E. Cross (1995) Thickness-dependent electrical characteristics of lead zirconate titanate thin films. J. Appl. Phys., 77(8), 3981-3986.

Yi, G., Z. Wu, and M. Sayer (1988) Preparation of Pb(Zr,Ti)O<sub>3</sub> thin films by sol-gel processing electrical, optical, and electro-optic properties. *J. Appl. Phys.*, **64**(5), 2717-2724.

# 水下技術所用鋯鈦酸鉛薄膜聲波元件的製作和量測

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# 摘要

本論文以射頻磁控濺鍍系統沈積鋯鈦酸鉛薄膜及結合積體電路製程技術於矽基板上製作水中聲波元件。而本論文所 沈積鋯鈦酸鉛薄膜之最佳沈積條件為基板350  $\mathbb{C}$ 退火溫度650  $\mathbb{C}$ ,退火時間20 分鐘,而所沈積的薄膜具有介電常數969, 介電損失0.3,矯頑電場0.061 Kv/cm,殘餘極化量112.5 nc/cm,而 $d_{33}$ 值為2.03 pm/v, $g_{33}$ 值為2.57 ×10<sup>-4</sup> vm/n,利用此 鋯鈦酸鉛薄膜,本實驗所製作之聲波元件可同時為發射接收元件最高的發射感度為76 dB 而最高接收感度為-75 dB,而由 實驗發現經極化後的鋯鈦酸鉛薄膜有較佳的元件特性。