Measurement of Longitudinal Piezoelectric Coefficients (d_{33}) of $Pb(Zr_{0.50},Ti_{0.50})O_3$ Thin Films with Atomic Force Microscopy

LIU Meng-wei[a], *DONG Wei-jie*[b], *TONG Jian-hua*[a], *WANG Jing*[b], *CUI Yan*[a],
CUI Tian-hong[a,c], *WANG Li-ding* [a]

[a]MST research center, School of Mechanical Engineering, Dalian University of Technology,Dalian,China
[b]Department of Electronic Engineering, Dalian University of Technology,Dalian, China
[c]Department of Mechanical Engineering, University of Minnesota, USA

ABSTRACT

Longitudinal piezoelectric coefficients (d_{33}) of sub-micro $Pb(Zr_{0.50},Ti_{0.50})O_3$ thin films were measured using an atomic force microscopy(AFM). The polycrystalline PZT films with (111) preferred orientation were deposited on $Pt/Ti/SiO_2/Si$ substrates using a modified sol-gel method. An optimized AFM-based method was proposed in this article, in which a grounded AFM tip contacted with the top electrode, and an ac voltage was applied between the top and bottom electrodes of the piezoelectric films. The electrostatic interaction between the tip and electric field was eliminated in the method. The piezoelectric films showed excellent linear piezoelectric deflection to the applied voltage. In order to quantify the piezoelectric coefficient of the PZT films, a standard X-cut quartz was used to calibrate the deflection of the AFM cantilever. The values of the d_{33} of a PZT film with 720nm thickness were14.1pm/V and 68.2pm/V for as-deposited film and the polarized film, respectively. Longitudinal piezoelectric coefficient of PZT crystal with 500μm thickness was measured using the AFM method and the traditional quasistatic method which is only used to measure the bulk ceramics, and d_{33} were 407.4pm/V and 420pm/V, respectively. The excellent coincidence indicates that reasonable piezoelectric constants can be yielded by the optimized AFM method.

Key words: longitudinal piezoelectric coefficient, atomic force microscopy, PZT, thin film, sol-gel

1. INTRODUCTION

In recent years, lead zirconate titanate (PZT) thin films have been vastly investigated for their applications to microelectromechanical systems (MEMS)[1~3]. Longitudinal piezoelectric coefficient d_{33} is an important parameter for piezo-MEMS devices. Traditional piezoelectric measurement techniques that are only used to measure the bulk ceramics, such as the resonance method and strain gauge method, are not suitable for films, because the films are always clamped to substrates. Several techniques have been attempted to measure the piezoelectric coefficient of PZT thin films based on the inverse piezoelectric effect, such as laser interferometry, atomic force microscopy and measuring the displacement of a cantilever. Compared to those techniques using the direct piezoelectric effect such as normal loading method[4], pneumatic loading method[5] and wafer flexure technique[6], they have the advantage of being able to measure the piezoelectric effect with high resolution[7].

The laser interferometer method is a well-established method for the characterization of piezoelectric coefficients of piezoelectric films. However, this method requires precise optical alignment and meticulous operation。Another limitation of the technique is the size of the top electrode of thin film has to be larger than the beam spot size that is typically a few millimeters. So it is not suitable for measurement of microstructure. The AFM technique has the advantages of being able to measure the piezoelectric coefficient at one point of a film and generate the piezoelectric image. Compared to macroscopic techniques mentioned above, AFM offers a significant advantage in studying piezoelectric properties of piezoelectric films at a nanoscale level. In this work, polycrystalline PZT films with (111) preferred orientation were deposited on $Pt/Ti/SiO_2/Si$ substrates using a modified sol-gel method. The piezoelectric measurement system was built using AFM, and longitudinal piezoelectric coefficients (d_{33}) of PZT films were measured.

2. PZT FILMS DEPOSITION

A PZT precursor solution (Zr/Ti = 50/50) was prepared using lead acetate trihydrate [$Pb(CH_3COO)_2 \cdot 3H_2O$], zirconium nitrate pentahydrate [$Zr(NO_3)_4 . 5H_2O$], and titanium tetrobutoxide [$Ti(O(CH_2)_3CH_3)_4$]. 2-methoxyethanol [$HOCH_2CH_2OCH_3$] and acetylacetone [$CH_3COCH_2COCH_3$] were used as the solvent and the chemical modifier, respectively. The coating solution of PZT films was deposited onto Pt(111)/Ti/SiO_2/Si(100) substrates by spin-coating at 4000 rpm for 30s. After each spin-coating process, the wet PZT thin film was baked at 200℃ on a hot plate for 5 min. A four-coated PZT thin film was obtained by repeating the coating and baking process for four times. Then the first annealing circle was produced by annealing the four-coated PZT film at 600℃ for 30 min by rapid thermal annealing (RTA) process in air. A process including four times spin-coating and pre-baking, one time post-annealing is called a coating and annealing circle. PZT thin films of 720nm thickness were received by repeating the coating and annealing circle for three times.

The phases and crystal orientations of the PZT films were examined by X-ray diffraction (XRD-6000, SHIMADZU, Japan). Fig.1 shows the XRD patterns of $Pb(Zr_{0.5}Ti_{0.5})O_3$ thin films deposited on Pt/Ti/SiO_2/Si substrates. It is indicated that the PZT films exhibited highly preferred orientation in the direction of the (111) plane. The ferroelectric properties of PZT films were measured using the TF Analyzer 2000 on FE mode at a frequency of 100 Hz. Fig.2 shows the *P-E* hysteresis loops of the PZT film with 720nm thickness, the film reveals obvious ferroelectricity.

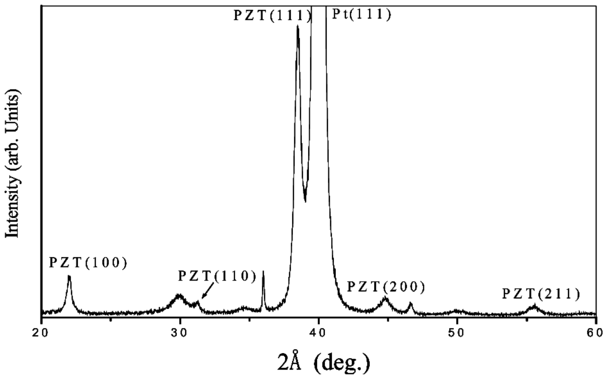


Fig.1 XRD pattern of PZT thin film deposited on Pt/Ti/SiO_2/Si substrate.

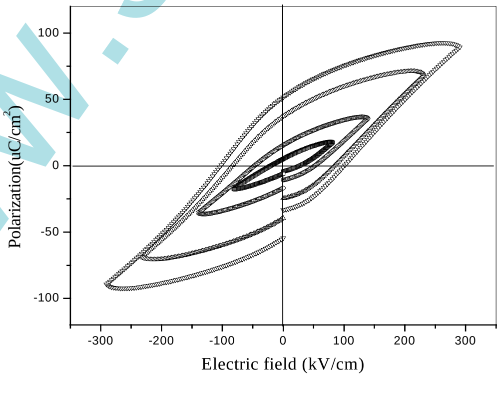
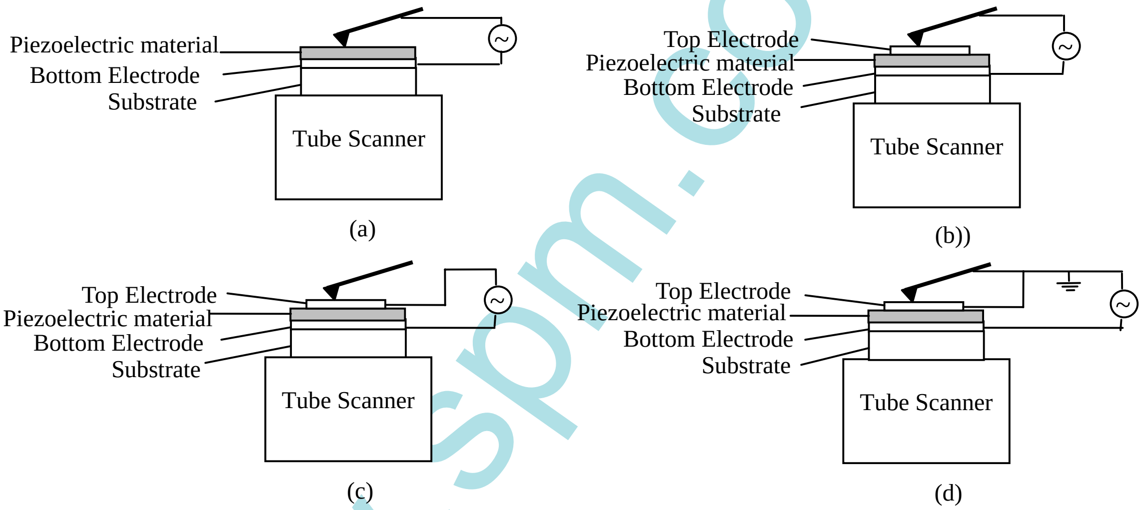


Fig.2 Ferroelectric hysteresis loops of the PZT film with 720nm thickness

3. MEASUREMENT OF POEZOELECTRIC COEFFICIENT d33

AFM measurements of the piezoelectric coefficient d_{33} utilize the converse piezoelectric effect of the piezoelectric materials. Measurements are performed in contact mode. When an ac electric field is applied to the sample, the AFM tip follows the piezoelectric motion. In order to measure the piezoelectric response at single point, the AFM scanner do not move in x and y directions. Measurements are performed in constant force mode with a small gain feedback. With the feedback, the tip can contact with the sample during long time measurement. The purpose of minimizing the feedback gain is to ensure that the AFM scanner does not respond to the piezoelectric motion in Z direction. When a piezoelectric sample is driven by an ac voltage at a frequency of f, the AFM tip displacement will be detected by a laser-photodiode combination system, and the voltage signal of the photodiode with frequency f will be recorded using a lock-in amplifier. The piezoelectric coefficient d_{33} can be determined by dividing the oscillation amplitude in thickness direction of the piezoelectric sample (from the AFM photodiode) by the driving voltage applied to the sample.

There are four different techniques used to AFM-based measurements of the piezoelectric effect, as shown in fig.3. The first technique is performed by applying an ac voltage between a conducting tip and the bottom electrode of the piezoelectric sample (as illustrated in fig.3(a)). In this case, the tip directly contacts with the piezoelectric material and acts as the top electrode. In the second technique (fig.3(b)), piezoelectric measurement is performed with a conducting tip in contact with a top electrode. Compared to the first technique, the piezoelectric excitation region can't be constrained by the surrounding material since the area of the top electrode is much lager than the area between the tip and the sample. In the third case (fig.3(c)), the AFM tip contact with the top electrode of the sample, and the ac voltage is applied between the two electrodes. The advantage of this technique is that the electric field driving the piezoelectric material can be more accurately determined than that applied by the conducting tip and the bottom electrode. Compared to the techniques mentioned above, the last one (fig.3(d)) is the best technique for measuring the longitudinal piezoelectric coefficient d_{33}. The top electrode of the piezoelectric sample and the conducting tip are grounded, which can reduce electrostatic interaction between the tip and electric field.



(a) (b))

(c) (d)

Fig.3 Four different techniques used to AFM-based measurements of the piezoelectric effect

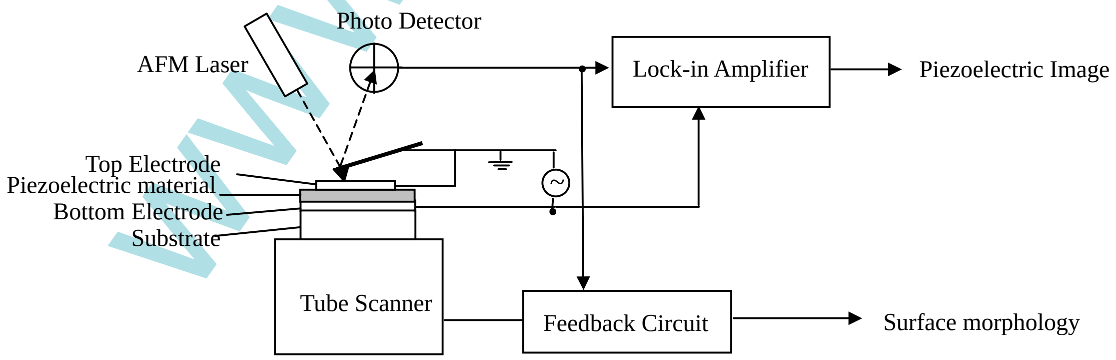


Fig.4 Schematic of the AFM setup for piezoelectric measurements

In this work, longitudinal piezoelectric coefficients (d_{33}) of PZT films were measured using the fourth AFM technique described above. Fig.4 shows schematic of the measurement system. An array of $1mm^2$ square Cr/Al top electrodes were sputtered onto the PZT films. Piezoelectric measurement system was built with a commercially available AFM (Benyuan CSPM-930b), a function generator (YB 1639), and a lock-in amplifier (EG&G 5209). A Ti-Pt conducting tip was used for piezoelectric measurement. The force constant and the resonant frequency of the tip are 6.0 N/m and 155kHz, respectively. An a.c. electrical signal, varying from 0 to 5Vrms was applied between the top and bottom electrodes of the piezoelectric films. The frequency of 1.27 kHz was employed, which is higher than most environmental noise frequencies and lower than resonance frequencies of both the tip and the sample. In our experiment, measurements were performed on five types of samples: 1) X-cut crystalline quartz (Φ20 x 1mm) which is served as a piezoelectric standard for the quantification of the piezoelectric coefficient; 2) Amorphous SiO_2 thin film (500nm thick) without a piezoelectric response; 3) as-deposited PZT film (720nm thick) prepared by sol-gel method; 4) poling PZT film under electric field of 15V at 100℃ for 1 h; 5) PZT crystal (500μm thick) which is used to calibrate the AFM-based piezoelectric measurement system.

4. RESULTS AND DISCUSSION

The lock-in reading as a function of applied voltage of several samples were measured using the optimized AFM technique (as illustrated in Fig.4) and the results are shown in Fig.5. Before these piezoelectric measurements, a non-piezoelectric SiO_2 thin film was measured for testing if the AFM tip interacts with the applied electric field on the samples. In this experiment, the lock-in amplifier signals were independent of the electric field and always at the experimental noise level, whether the AFM tip is in contact with the top electrode, or above the top electrode. This result indicates that the tip oscillation in piezoelectric measurements is due to piezoelectric motion, rather than the tip-sample electrostatic interaction. All the piezo-samples exhibit excellent proportional relationship between the piezoelectric displacement and the applied voltage, as shown in fig.5.

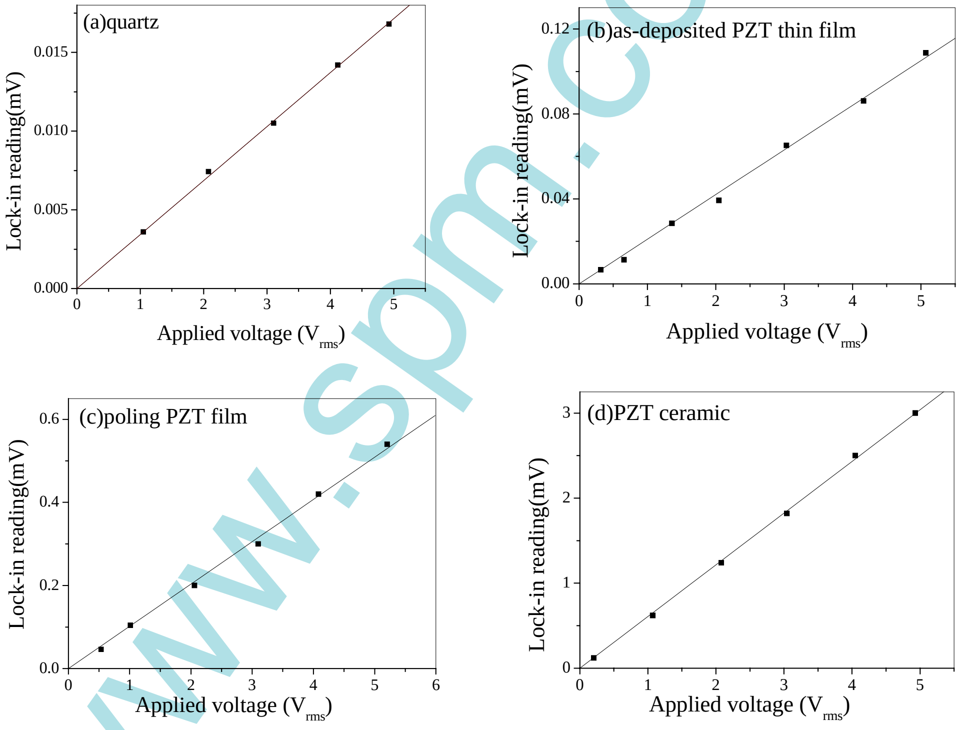


Fig.5 The lock-in reading as a function of the applied voltage of several samples

The piezoelectric displacement was calibrated using a X-cut crystalline quartz, which has a constant d_{11}, 2.3pm/V. The slope of the curve in fig.5(a) leads to a conversion constant between the voltage signal of the AFM photodiode (the locking-in reading) and the inverse piezoelectric induced displacements. The longitudinal piezoelectric coefficients d_{33} for PZT films can be calculated as follows:

$$d_{33} = \frac{slope(film) * d_{11}(quartz)}{slope(quartz)}, \quad slope = \frac{lock\_in\_reading}{V_{AC}}$$

where V_{AC} is the voltage applied between top and bottom electrodes of piezoelectric samples. The longitudinal piezoelectric coefficients d_{33} of three samples are calculated and shown in table 1. The as-deposited PZT thin film has spontaneous piezoelectric response without the polarized process that is necessary to PZT ceramic.

After the PZT film was polarized under electric field of 20.8V/μm at 100℃ for 1 hour, the d_{33} increased from 14.1pm/V to 68.2pm/V. It is indicated that the poling process has a great effect on the piezoelectric property of the PZT films.

Table 1 longitudinal piezoelectric coefficients of PZT films and PZT ceramic

Samples	**Quartz (standard)**	**PZT films (720nm thick)**		**PZT ceramic (500μm thick)**
		As-deposited	polarized	
Slope (mV/V)	0.00343	0.0210	0.102	0.608
d_{33} (pm/V)	2.3	14.1	68.2	407.4

The piezoelectric constant d_{33} of PZT ceramic (500μm thick) measures by the AFM method was 407.4pm/V, as listed in table 1. In order to calibrate the AFM-based piezoelectric measurement system, the same specimen was measured using the quasistatic piezoelectric d_{33} meter (ZJ-3D, Institute of Acoustics, Chinese Academy of Sciences), which are based the direct piezoelectric effect. The d_{33} was 420pC/N(pm/V). This excellent agreement supports the validity of the present AFM piezoelectric measurement method.

5. CONCLUSION

We evaluated the longitudinal piezoelectric coefficients of the PZT films by an optimized AFM method. A non-piezoelectric SiO_2 thin film was measured using the AFM method, which verified no electrostatic interaction existed between the tip and sample. PZT films with (111) preferred orientation were prepared by a modified sol-gel method. All the piezoelectric samples showed excellent linearity of piezoelectric displacement to the applied voltages. The d_{33} of as-deposited and poling PZT films of 14.1pm/V and 68.2pm/V were obtained using the AFM-based piezoelectric measurement method. The d_{33} of PZT ceramic obtained by the AFM method was compared to the value measured by the conventional method, which indicated that the reasonable piezoelectric constants could be yielded by the optimized AFM method.

6. ACKNOWLEDGEMENTS

This paper is supported by the National Natural Science Foundation of China (No.90207003).

REFERENCES

[1] S Zurn, M Hsieh, G Smith, D Markus, M Zang, G Hughes, Y Nam, M Arik and D Polla. Fabrication and structural characterization of a resonant frequency PZT microcantilever. Smart Materials and Structures. 2001,10:252-263

[2] Li-Peng Wang, Wolf R.A. Jr., Yu Wang, Deng K.K., Zou L., Davis R.J., Trolier-McKinstry S. Design, fabrication, and measurement of high-sensitivity piezoelectric microelectromechanical systems accelerometers. Journal of Microelectromechanical Systems. 2003,12(4):433-439

[3] Lee Chengkuo, Itoh Toshihiro, Suga Tadatomo. Self-excited piezoelectric PZT microcantilevers for dynamic SFM-with inherent sensing and actuating capabilities. Sensors and Actuators A: Physical. 1999,72(2):179-188

[4] Ren W., Zhou H.-J., Wu X.-Q., Zhang L.-Y., Yao, X.. Measurement of piezoelectric coefficients of lead zirconate titanate thin films by the normal load method using a composite tip. Materials Letters. 1997,31:185-188

[5] Gun-Tae, Choi Jong-Jin, Ryu Jungho, Fan Huiqing, Kim Hyoun-Ee. Measurement of piezoelectric coefficients of lead zirconate titanate thin films by strain-monitoring pneumatic loading method. Applied Physics Letters. 2002,80(24):4606-4608

[6] Shepard Jr., Joseph F., Chu Fan. Characterization and aging response of the d31 piezoelectric coefficient of lead zirconate titanate thin films. Journal of Applied Physics. 1999,85(9):6711-6716

[7] Liu J.-M., Pan B., Chan H.L.W., Zhu S.N., Zhu Y.Y., Liu Z.G. Piezoelectric coefficient measurement of piezoelectric thin films: an overview. Materials Chemistry and Physics. 2002,75(1-3):12-18

contact.Liu Meng-wei, e-mail:liumengwei@student.dlut.edu.cn; phone: 0411-84707713-8107; fax:0411-84707940; Address: MST research center, School of Mechanical Engineering, Dalian University of Technology, Dalian 116023,China