

REACTIVE SPUTTER DEPOSITION OF PZT THIN FILMS FOR RESONANCE FREQUENCY TUNING OF MEMS VIBRATION ENERGY HARVESTER

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Abstract: This paper describes the reactive sputter deposition of the Lead Zirconium Titanate (PZT) thin film using pulsed DC sputtering for resonance frequency tuning in vibration energy harvesting devices. Finite element modeling showed higher relative shift in frequency for PZT films compared to AlN films. After rapid thermal annealing (RTA) the PZT thin films, showed a maximum dielectric constant of 970, with a remanent polarization of $27\mu\text{C}/\text{cm}^2$ and a coercive field of $45\text{kV}/\text{cm}$. For the Pt bottom electrode different type of adhesion layers, namely Ti and TiO_2 , were examined for PZT growth. The crystalline orientation was examined by X-ray Analysis (XRD) for different anneals. Furthermore the dielectric and ferroelectric properties of the different layers were investigated.

Keywords: piezoelectric, frequency tuning, Lead Zirconium Titanate (PZT), reactive sputtering

1 INTRODUCTION

Piezoelectric thin films forms an integral part of MEMS vibrational energy harvesting devices. In such conventional devices, there exists a potential mismatch between resonance frequency and external vibration frequency, which can be addressed by changing the resonance frequency of the harvester through actuation [1]. In the current approach, an electric field applied across free standing piezoelectric thin film placed on either side of the silicon beam (Fig.1), induces mechanical stress, causing the film to curl upwards and increases the bending stiffness of the beam, resulting in a frequency shift.

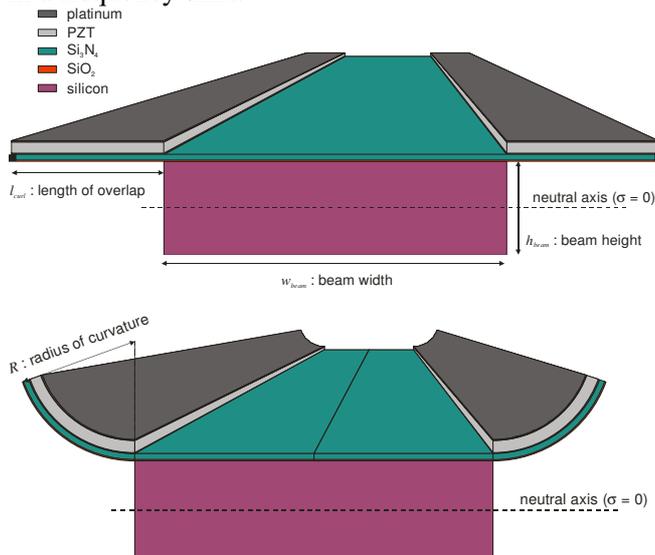


Fig. 1. Sketch of a silicon beam with free standing thin films which carry a piezoelectric material and electrodes (not to scale). The piezo-stack is intended to stress the thin film and thus curls the overlapping material upwards (second picture). The deformation is due to stress generated by the piezostack and increases the bending stiffness of the beam.

Aluminum nitride (AlN) is a suitable piezoelectric material used in MEMS based vibration energy harvesters [2], but AlN is not suitable for actuation due to its low piezoelectric constant e_{31} . Another example of a piezoelectric material is Lead Zirconium Titanate (PZT), for which the high e_{31} values [3] make this a suitable material for frequency tuning.

Finite element modeling showed a relative frequency shift up to 25% for PZT based tuning actuator by varying the length of free standing thin film (Fig. 2).

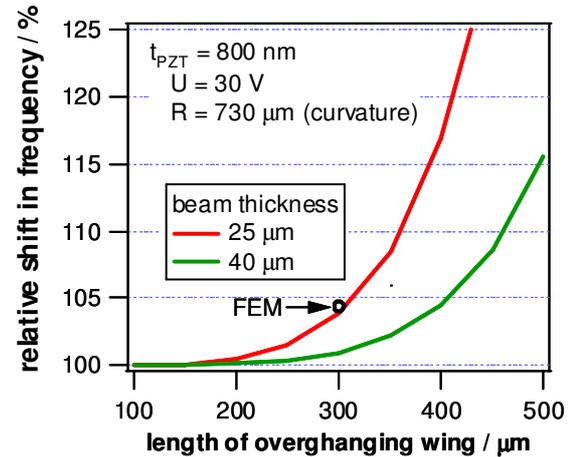


Fig. 2. Modeling result showing the achievable shift in frequency using a silicon beam of 7 mm width and a PZT-based tuning actuator for different silicon beam thickness. For one configuration, the calculated result is compared with finite element modeling (FEM).

In comparison AlN only showed 0.1% frequency shift. This urged the development of high quality PZT thin film deposition technique for resonance frequency tuned energy harvesting devices.

2 EXPERIMENTAL PROCEDURES

2.1 Film Deposition

The PZT thin films were deposited by reactive sputter deposition using pulsed DC power. A 12'' circular single metallic target with 6mm thickness was mounted in the reaction chamber. The target composition of (at %) Pb (55) Zr (22.5) Ti (22.5) was adjusted in order to compensate for the Pb losses by evaporation, which occurs at higher temperatures. Layers were deposited on thermally oxidized silicon wafer with a TiO₂/Pt and Ti/Pt stack at 475°C. A DC Power of 1.5kW with frequency of 100 kHz and 80% duty cycle was employed.

A reactive gas mixture of argon and oxygen was introduced at 20mTorr, with a controlled partial pressure of oxygen. The target voltage was constantly monitored in order to make sure that target is not poisoned, which could lead to unstable plasma. [4]

2.2 Investigation of the bottom electrode layer

For electrode materials, Ti/Pt is often used for PZT thin film deposition, because Pt is a noble metal and an excellent conductor. Titanium enhances the adhesion between the platinum electrode and the barrier thermal oxide layer. The major problem associated with using platinum as a bottom electrode is the interaction with the titanium adhesion layer during the post-annealing treatment of the PZT films [5]. To investigate the substrate evolution during the post annealing of PZT, the surface morphology of Si/SiO₂/Ti/Pt stack with and without annealing was compared. The surface morphology showed a distinguished difference between the annealed and non annealed bottom electrode stack. For the annealed layers at 600°C for 5min, there is oxidation of the intermediate Ti layer and its migration into Pt layer. Some Ti atoms reach the top surface of the Pt layer and get accumulated there. It is also evident from the undefined boundary between the Pt and Ti layer. EDS analysis on these layers also revealed the presence of Ti on the surface. The Pt layer, encapsulated with a thin non continuous Ti layer (Fig: 2.b), can induce hillock and micro crack formation on the top PZT layer.

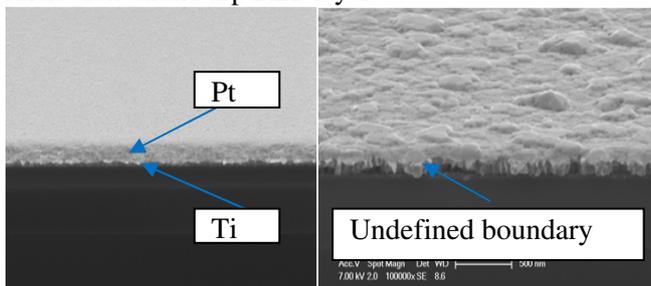


Fig 2: Ti/Pt before (a) and after (b) RTA at 600°C for 5min

These experiments clearly indicate that, the bottom electrode stack undergoes drastic changes during

annealing and could degrade the PZT film growth. In order to have a stabilized bottom electrode layer, the growth condition of Ti is altered by introduction of oxygen, so as to form TiO₂ beneath Pt layer.

Using an appropriate annealing method; single or mixed TiO₂ phase can be formed. [6,7]. The thermal stability of TiO₂/Pt layer is analyzed for its surface properties before and after annealing. Surface property of as deposited as well as the one with RTA at 800°C for 10min on TiO₂/Pt layer didn't exhibit significant differences, making it an appropriate candidate for PZT deposition.

2.3 Rapid Thermal Annealing and Characterization

Rapid thermal annealing was performed on the sputtered PZT wafers, in order to check the orientation of the film X-Ray diffraction analysis (XRD) is used. Stoichiometric and surface morphology analysis was also performed by Energy Dispersion spectroscopy (EDS) and Scanning electron Microscopy (SEM).

Rapid thermal annealing was done on the film for temperatures between 650 and 750°C for 10s. RTA temperature and duration was carefully chosen, as higher temperature or longer duration could degrade the film structure due to evaporation of Pb [8].

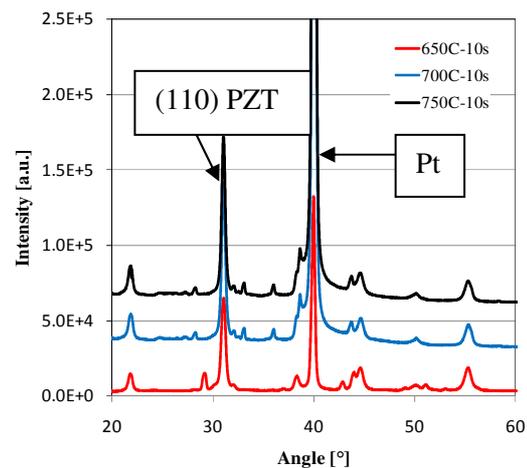


Fig 3: XRD Spectra of RTA samples

XRD showed the presence of sharp perovskite (110) peaks for all the annealing temperatures. Apart from that, polycrystalline (100) and (200) peaks of smaller intensity were also present, which might be due to the deviation from morphotropic phase boundary region (Fig. 3). Generally, the orientation of PZT is not controlled on Pt (111) bottom electrode, as PZT (111) or (110) can be obtained. This phenomenon was related to surface quality of Pt layer [9, 10]. The (111) oriented PZT is obtained, when there is formation of Pt₃Ti at the interface due to diffusion of TiO₂ on Pt surface during RTA. This normally occurs, when excess Ti cations are present [11]. In our case, the annealed bottom electrode (TiO₂/Pt) didn't exhibit any TiO₂ presence on top of Pt layer, when examined by EDS as well as with XRD before PZT deposition.

This correlates with the presence of sharp (110) PZT peak.

Another parameter that promotes (110) growth is that the lattice mismatch between, Pt (111) and PZT (Zr/Ti=50/50) being more than 4%. This induces a lattice misfit strain and affects the nucleation rate of (111) PZT. [12]

The composition analysis by EDS on PZT showed a decrease in percentage of PbO, as the temperature is increased to 800°C, which is quite evident from the low vapor pressure of Pb at high temperature causing evaporation and resulting in the formation of Pb-deficient pyrochlore or fluorite intermediate phases [13].

Moreover, the diffusion of Pb from the PZT film into the Pt electrode has been reported under certain conditions to form a $PbPt_x$ ($x=5-7$) phase which also contributes to the Pb loss and also aids in nucleation of PZT (110) columnar crystals [14].

Pb/ Zr+Ti ratio of the target determined by EDS, was 1.22 and the samples annealed at various temperatures (650-750°C) had a ratio of between 1.1-1.06 (Table 1), which is nearly equal to the desired value of 1.0. The Zr and Ti concentrations of the samples annealed from 650 to 750°C, were also comparable to the desired value. Samples annealed at 800°C for 10s had a ratio of 0.92, below the desired value. They also had a significant PbO loss, which might result in the

degradation of the films physical properties. Examining the structure morphology by SEM, a homogeneous, dense, crack free grainy surface has been observed for as deposited PZT samples, with a grain size of approximately 85nm on the TiO_2/Pt layer. After RTA, the surface becomes relatively smooth. The cross section of the films annealed at 750°C for 10s, reveal columnar growth, usual for a PZT film. The grain size increased to 100 - 120nm. (Fig: 4)

As the temperature is increased above 800°C, we notice less dense packed morphology with holes and cracks in the film, attributed to Pb loss. Hence this confirms that, RTA treatment has to be limited below 800°C.

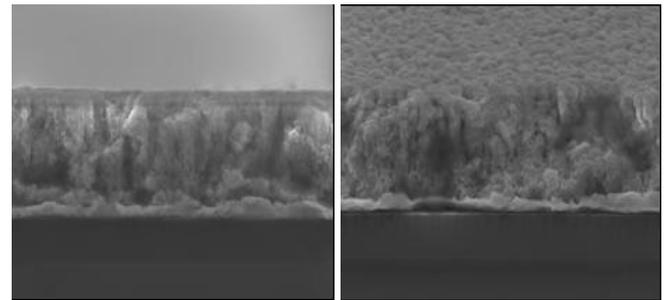


Fig.4: Cross section of the sample after RTA at 750°C for 10s

Sample	Pb (at %)	Zr (at %)	Ti (at %)	O (at %)	Pb/(Zr+Ti)	PbO %
PZT Actual	20	10.4	9.6	60	1	-
PZT as Deposited	18.88	8.05	8.12	64.93	1.16	16.71
RTA-650°C, 10s	23.29	10.54	10.49	55.65	1.1	10.65
RTA-700°C, 10s	23.74	11.5	10.58	54.1	1.07	7.4
RTA-750°C, 10s	23.69	11.2	11.0	54.0	1.06	6.42
RTA-800°C, 10s	21.7	11.94	11.44	54.9	0.92	-7.2

Table 1: Pb/Zr+Ti ratio and PbO% determined by EDS (Pb / Zr+Ti = 1.22 in target)

3 DIELECTRIC AND FERROELECTRIC PROPERTIES

A top platinum electrode was sputter deposited on PZT and patterned by dry etching to facilitate electrical measurements. Capacitive measurements showed a maximum dielectric constant of 970 and a loss factor of 5% for 1 μ m films of 0.64mm² annealed at 750°C for 10s.(Fig. 5)

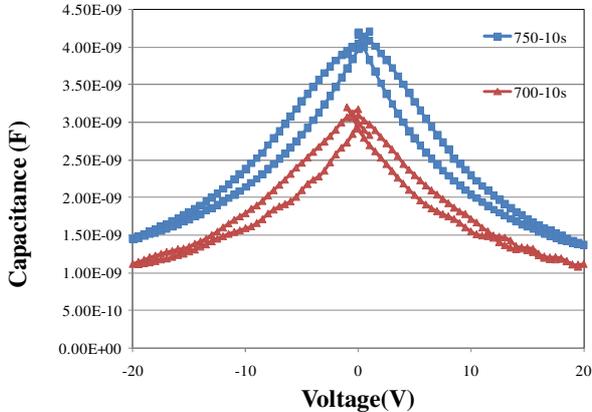


Fig.5: Capacitance - voltage sweep from zero to negative and then from zero to positive

The ferroelectric nature of the films was examined at room temperature with 200Hz frequency by means of a Sawyer-Tower circuit [15]. Ferroelectric polarization values and coercive fields are measured as functions of applied voltage for different RTA treated 1 μ m PZT films with rhombohedral-tetragonal (Zr/Ti = 50/50) composition (fig: 6). RTA sample at 650°C -10s, exhibited low saturation polarization of 24 μ C/cm², compared to 30 and 32 μ C/cm² for 700 and 750°C annealed samples.

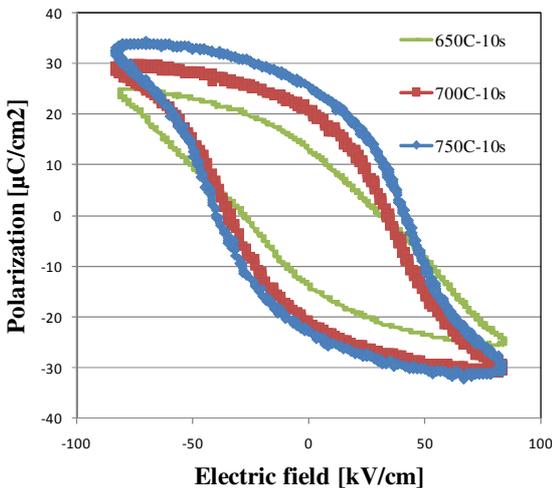


Fig. 6: P-E Hysteresis Loop at 10V applied voltage

With increasing temperature, larger remanent polarization and higher coercive fields are observed, while the difference between saturation and remnant polarization becomes smaller. From the above observation, it is apparent that the PZT films annealed at 750°C display switching characteristics most similar to those of ideal single crystals. The P-V hysteresis loops of PZT films with higher annealing temperature

show sharper switching behavior, normally seen in rhombohedral phase. Meanwhile, the square P-V hysteresis loops have not been obtained for 650°C annealed sample, despite a good degree of orientation. The explanation for this behavior is that, once we go to higher annealing temperatures, the grain size increases to few ten's of μ m, facilitating 180° domain wall motion and less domain wall pinning. [15]

4 CONCLUSION

We have deposited high quality PZT thin film using pulsed-dc reactive sputtering for the use in resonance frequency tuning of vibration energy harvesters. The bottom electrode layer of TiO₂/Pt was chosen for the PZT film growth, due to its thermal stability compared to Ti/Pt layer. The PZT films showed comparable dielectric constant of 970 and remanent polarization value of 27 μ C/cm² for the 1 μ m films annealed at 750°C for 10s. At the moment transverse piezoelectric coefficients of sputtered PZT are being measured on 4-point bending structures [16]. These values are needed for the calculation of the coupling coefficient figure of merit and enabling comparison with literature values for PZT and other piezoelectric materials. Future work will involve in fabrication of frequency tuned energy harvesters with the reactive sputtered PZT thin film.

REFERENCES

- [1] D. Zhu et al., *Meas. Sci. Technol.* 21, 022001, 2010
- [2] R.Elfrink et al., *Journal of Micro Mech Micro Eng.*,19, pp-094005,2009
- [3] S.Trollier McKinstry and P.Muralt, *Journal of Electroceramics* 12, pp 7-17, 2004
- [4] Anders.A, *Thin Solid Films*, vol. 502, pp. 22-28,'06
- [5]G.R.Fox et al., *Journal of Material Research*.vol.10, pp-1508, 1995.
- [6] Martin, et al., *Thin Solid Films* vol- 287, pp- 154-163, 1997
- [7] Martin et al., *Thin Solid Films* vol-300, pp-113-121, 1997
- [8] C. C. Chang, et al., *Journal of Material science-Materials in electronics*, vol-10, pp- 551- 556, 1999.
- [9] L. Jiankang et al., *Material Letters*, Vol-58, pp-3447-3450, 2004
- [10] C. Millon et al., *Sens. Actuators A*, vol-113 pp-376-381, 2004.
- [11] T. Tani et al., *Mater. Res. Soc. Symp. Proc.* 310 (1993) 269-274
- [12] Seung-Hyun Kim et al., *Japanese Journal of Applied physics*, vol-42, pp-5952, 2003
- [13] G.Velu et al., *Journal of Vacuum*, vol-56, pp-199-204,2000.
- [14] A. Impey et al., *J. of App. Phys.* 83, 2202 (1998)
- [15] K. Srinivas et al., *Journal of applied physics*, vol-64, pp-1484, 1988.
- [16] K. Prume et al., *IEEE transactions on Ultrasonics, Ferro electricity and Frequency Control*, 54 pp. 8-14, 2007