Microsystem Technologies 10 (2004) 137–141 © Springer-Verlag 2004
DOI 10.1007/s00542-003-0319-6

Piezoelectric thin films formed by MOD on cantilever beams for micro sensors and actuators

T. Cui, D. Markus, S. Zurn, D. L. Polla

Abstract Novel piezoelectric cantilever beams for micro sensors and actuators based on PZT thin films have been batch fabricated by surface micromachining. Lead zirconate titanate (PZT) thin film is formed by metalorganic deposition (MOD) on $Pt/Ti/SiO_2/Si$ (1 0 0) substrates and $Pt/Ti/LTO/Si_3N_4$ cantilever beams and then annealed at 700 °C in air. The PZT thin film is 0.5 μm thick and has dielectric permittivity of 1698, remanent polarization of 13.66 $\mu C/cm^2$, and coercive field of 44.5 kV/cm. The influence of deposition temperatures on PZT thin film stress has been investigated. When continuously controlling the deposition temperatures, the stress of the thin film is reduced from 0.313×10^8 to 0.269×10^8 N/m, that is 16.4% decrease. With the total 120 designed devices on 4-inch wafers, the number of functional devices is increased from 82 to 97, that is 12.47%.

1 Introduction

PZT thin films have been intensively investigated since they offered promising piezoelectric and ferroelectric properties that can be applied to microelectronic, optoelectronic, and micromechanical devices [1, 2]. Recently the PZT thin film has attracted more attention to its applications to microelectromechanical systems (MEMS) due to its desirable properties such as spontaneous polarization, high piezoelectric constant, and pyroelectricity [3–5]. There are several methods to deposit PZT thin films such as sol–gel process which was employed to fabricate ultrasonic micromotors [6], hydrothermally synthesized PZT films which were deposited on metal to form bimorph cantilever [7], screen printing PZT for dynamic micropumps [8], sputtering [9], laser ablation [10], electron beam deposition [11], ion beam deposition [12], metalorganic chemical vapor deposition (MOCVD) [13, 14], and metalorganic decomposition (MOD) [15]. Here MOD is defined as a metalorganic deposition method to spin-coat a PZT solution on substrates, then to cure and anneal the PZT thin films by heating the substrates. The precursors of MOD PZT are metalorganic materials different from that of sol–gel. The precursors of MOD PZT are less harmful compared to that of sol–gel PZT. Among all the techniques, the MOD method appear to be most promising in the area of MEMS because it offers the advantages of simplified apparatus, excellent film uniformity, good composition control, high film density, high deposition rate, excellent step coverage, and amenability to large scale processing. However, currently very few reports are available on MOD PZT films for MEMS applications. At present cracking of the MOD PZT film is the most serious problem to delay the applications of MOD PZT thin films to micro devices. In contrast, the unique aspects of this research are the following: (1) Novel MOD procedures to fabricate MOD PZT thin films on $Pt/Ti/SiO_2/Si$ (1 0 0) substrates and $Pt/Ti/LTO/Si_3N_4$ cantilever beams, (2) Measurement of curvature change to characterize the stress of PZT thin films, and (3) Demonstration of functional piezoelectric cantilever beams based on MOD PZT thin films to verify the process improvement.

Our primary objective to investigate MOD PZT thin films is to batch-fabricate piezoelectric cantilever beams for microsensors or microactuators, such as piezoelectric accelerometers, micro force sensors, micropumps, active valves, micromotors, etc.

Received: *20 August 2002 / Accepted*: *27 March 2003*

T. Cui (✉)
Institute for Micromanufacturing, Louisiana Tech University
911 Hergot Avenue, Ruston, LA 71272, USA
E-mail: tcui@coes.latech.edu

D. Markus, S. Zurn, D. L. Polla
Department of Electrical and Computer Engineering,
University of Minnesota, Minneapolis, MN 55455, USA

Tianhong Cui joined the faculty of Institute for Micromanufacturing at Louisisana Tech University in 1999. He received his B.S. from Nanjing University of Aeronautics & Astronautics in 1991, and his Ph.D. from Chinese Academy of Sciences in 1995. He has conducted research and development work for the realization of microsensors and microactuators since 1992. Prior to joining the IfM in 1999, he was at the National Laboratory of Metrology in Japan as a Research Fellow under STA fellowship, and previous to that, served as a Postdoctoral Research Associate at the University of Minnesota. His current research interests include MEMS, polymer micro/nanoelectronics, and nanotechnology.

2 Fabrication

2.1 Modified MOD for PZT deposition

For PZT layers, the modified MOD to form PZT thin films on top of silicon substrates and cantilever beams has been carried out. The PZT thin film deposition is the most critical technique to fabricate successful piezoelectric micro devices, while the selection of PZT precursors is the first important step. Here the precursors are chosen as the following: titanium isopropoxide, zirconium acetoacetonate, and lead acetate. A PZT layer will be formed by a MOD spin-coating process. The base solution used in the MOD spin-coating can be formed by the following steps: (a) pipette 5.344 g Titanium Isopropoxide into a flask, (b) add 16.128 Glacial Acetic Acid, (c) add 10.688 ml DI water, (d) put 10.338 g Zirconium Acetoacetonate and 16.69 g Lead Acetate in to the flask, (e) add DI water to bring the total volume to 50 ml, and (f) add 1.742 g 30% H_2O_2 and shake for 1 h. The previous MOD PZT thin film was spin-coated at 125 and 425 °C, and annealed at 700 °C discontinuously. To reduce the cracking of PZT thin films, the casting temperatures in our experiments are controlled continuously. After PZT solution is spin-coated, the MOD casting and annealing conditions to deposit PZT thin films are listed in Table 1. The MOD PZT composition is approximately Pb(Zr, Ti)O_3. The ratio between Zr and Ti is close to 1:1, making the PZT thin film to be crystalline bonding structures.

2.2
Fabrication of piezoelectric cantilever beams

Figure 1 shows the main steps to fabricate piezoelectric cantilever beams. First, etch cavities on a silicon water using RIE dry etching. Next, a layer of PSG is deposited by LPCVD and patterned inside the cavities, as shown in (A). After that, Si_3N_4 and LTO SiO_2 are deposited on top of PSG by LPCVD again, as shown in (B). Then deposit Ti and Pt as the bottom electrode, and coat PZT layers by modified MOD. Following that, deposit another layer of Pt as the top electrode, as shown in (C). After all of above deposition, pattern the substrate from top to bottom to etch the top electrode, the PZT layer, the bottom electrode, as shown in (D). Finally, etch LTO SiO_2 and Si_3N_4 to release the cantilever beams, as shown in (E).

3
Experiments

3.1
Stress measurement of PZT thin films

To prepare for the samples for stress measurements, the following process is used to fabricate PZT thin films on 4-inch Si (1 0 0) wafers. First, clean silicon wafers using RCA method. Next 500 nm SiO_2 is deposited on silicon wafers. After that, 10 nm titanium as an adhesion layer of platinum is deposited on SiO_2, and 150 nm platinum as the bottom electrode is evaporated on top of titanium by e-beam evaporation. As the above the modified MOD procedures in Table 1, PZT is coated on the bottom electrode (Pt) 4 times to obtain 0.5-μm-thick films. Anneal the PZT films at 700 °C in furnace for 1 h. Finally, another layer of 100 nm platinum as the top electrode is deposited by e-beam evaporation. The above entire wafers with 0.5 μm PZT thin films will be used as the samples for stress measurement of PZT thin films.

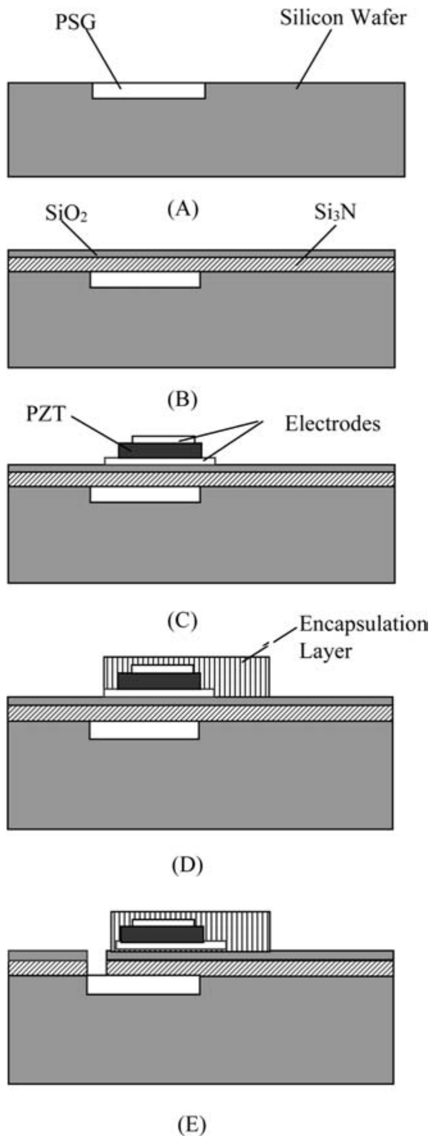

Fig. 1. Main steps to fabricate piezoelectric cantilever beams

Table 1. Summary of modified MOD casting and annealing conditions to deposit PZT thin films (Substrates: Pt/Ti/SiO_2/Si (1 0 0) wafers and Pt/Ti/LTO/Si_3N_4 cantilever beams)

Process name/critical parameters	Process conditions
First step	Heat the substrates from room temperature to 125 °C, and keep 125 °C for 10 min
Second step	Heat the substrates from 125 to 425 °C, and keep 425 °C for 10 min
Annealing and its temperature control	Heat the substrates from 425 to 700 °C, then anneal at 700 °C for 1 h, and finally cool down generally to room temperature
Annealing atmosphere	1 atm
Annealing period	1 h

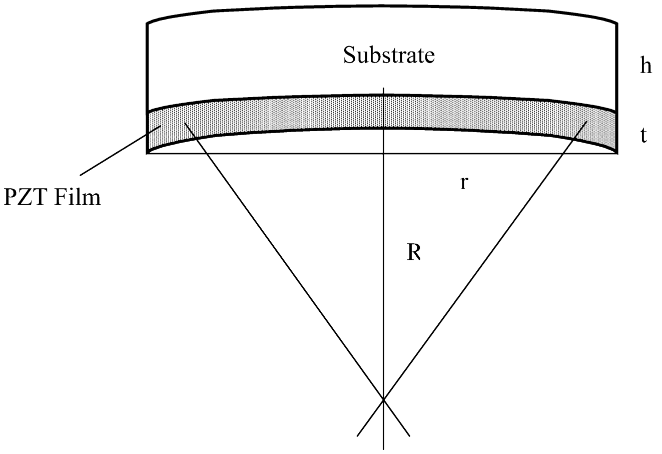

Fig. 2. Principle of a PZT thin film stress measurement

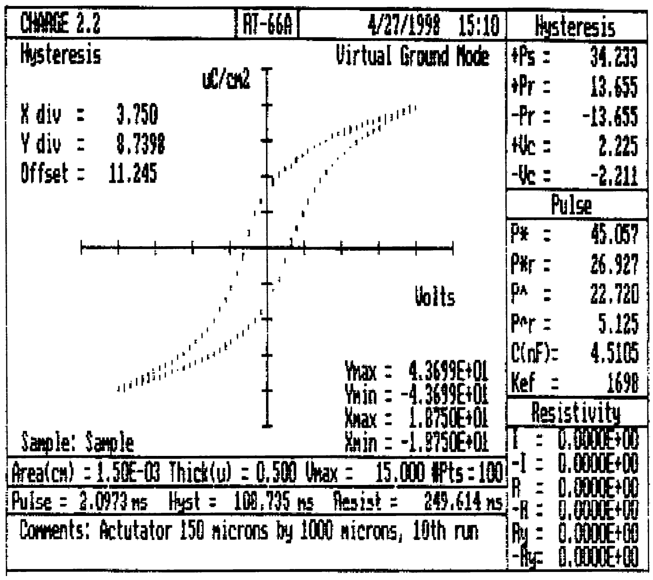

Fig. 3. Hysteresis loop of a PZT thin film by modified MOD

To examine the stress of PZT thin films, Microsense 3114A-385 (Wafer Bow) is used to test the above samples. The principle of the stress measurement is shown as Fig. 2. The contact sensor will measure the relative vertical positions of the wafer center and six points along the wafer rim before and after the film deposition. Due to the internal stress of the PZT crystallization, the stress will change the bow of the wafer before and after the PZT deposition. The stress of PZT thin films is defined as

$$\sigma = \frac{(E/(1-v)) \cdot h^2}{6Rt} \quad (1)$$

$$R = r^2/2\Delta_{\text{gradient}} \quad (2)$$

$$\Delta_{\text{gradient}} = [\text{center} - \text{arg} \cdot \text{side}]_{\text{after}} - [\text{center} - \text{arg} \cdot \text{side}]_{\text{before}} \quad (3)$$

where σ is the stress of PZT thin films, E is the Young's modulus, v is the Poisson's ratio, h is the wafer thickness, R is the effective radius of curvature ball, t is the film thickness, r is the span of measurement circle, Δ_{gradient} is the change in the bow of the wafer before and after the PZT deposition, center $-$ arg $\cdot$ side is the height or vertical position difference between the center and side average (the average relative height of the six points along the wafer rim).

After the bottom electrode Pt is deposited, the center and seven side points of the wafer are tested by Microsense 3114A-385. After the PZT is coated and annealed, the center and the same edge points are measured again. The stress can be calculated from Eqs. (1)–(3). Two types of samples have been prepared. One kinds of samples are based on the previous MOD method by discontinuously controlling temperatures, the others are by the procedures in Table 1 by continuously controlling temperatures. When continuously adjusting the casting temperature, the stress of thin films is from 0.313×10^8 to 0.269×10^8 N/m, that is 16.4% decrease.

Figure 3 shows the hysteresis loop that indicates the dielectric and piezoelectric properties of modified MOD PZT thin films using RT66 A. For the MOD based on the continuously controlled temperatures, the 0.5-μm PZT thin film has dielectric permittivity of 1698, remanent polarization of 13.66 μC/cm^2, and coercive field of 44.5 kV/cm. While for the same 0.5 μm PZT thin films using MOD but the discontinuously controlled temperatures, the dielectric permittivity is 1263, remanent polarization of 11.40 μC/cm^2, and coercive field of 57.9 kV/cm. That is to say, after the MOD process is modified, the properties of PZT thin films are improved. Table 2 lists the properties of PZT thin films based on different fabrication techniques. The remanent polarization and the coercive field of modified MOD PZT film are comparable to previously reported values by other deposition methods. This indicates that the PZT thin film formed by modified MOD has the same composition and crystalline structures as the PZT deposited by other techniques. The dielectric permittivity of the PZT thin film by modified MOD is much higher than the PZT by other techniques. There are two

Table 2. Properties of PZT thin films by different fabrication techniques

Deposition methods	Dielectric permittivity	Remanent polarization (μC/cm^2)	Coercive field (kV/cm)
Sol–gel [6]	130	36	30
Hydrothermally Synthesis [7]	380	–	–
Sputtering [9]	900	10	23
MOCVD [14]	–	12.3	64.5
MOD [15]	1263	11.40	57.9
Modified MOD	1698	13.66	44.5

possible reasons to support this remarkable differences. The continuous temperature control probably makes the PZT thin film more condense than the PZT formed by other techniques. The limited residual organic components may contribute to the increase of dielectric permittivity. Usually organic materials or components have higher dielectric permittivity than other general materials or components.

3.2
Piezoelectric cantilever beams

To test the cracking reduction of modified MOD PZT thin films, surface micromachining is carried out as the key technique to fabricate piezoelectric cantilever beams. The mechanical structure is formed with a low thermal mass and low thermal conductivity to the underlying substrate. A patterned 2 μm phosphosilicate glass (PSG) film is used to define the air gap of the microstructures. 3 μm low stress silicon nitride is deposited and patterned over PSG with holes for etching. The lateral dimensions of low stress silicon nitride is 300 μm by 1000 μm. Low thermal oxide 500 nm thick is deposited as the adhesion layer of titanium. The next layers are titanium and the bottom electrode platinum evaporated by e-beam evaporator. Then the MOD PZT thin film and top electrode platinum are deposited. The top and the bottom electrodes are etched by ion milling, while the PZT thin film is etched by wet chemical etching. Another layer of PECVD silicon oxide is deposited as the isolation layer between the top and the bottom electrodes of the PZT thin film. Aluminum with lateral dimensions of 500 μm by 500 μm is evaporated and patterned as the bonding pads. A layer of 1 μm silicon nitride by PECVD is used as the encapsulation layer. Lateral etching of PSG layer using hydrofluoric acid vapor is carried out to form the membranes for cantilever beams. Finally, RIE is used to remove the encapsulation layer to release the cantilever beams.

The cantilever beams 1000 μm long, 300 μm wide, and 3.5 μm thick have been batch-fabricated successfully, SEM photographically shown in Fig. 4. On each wafer, 120 cantilever beams have been designed and fabricated. Continuously and discontinuously controlling casting temperatures are both used, while coating MOD PZT thin films on two types identical wafers, in order to compare with each other about the internal stress and cracking. Every cantilever beam has been tested on the two types wafers. While the other situations are all the same, cantilever beams on 10 wafers by modified MOD and 10 wafers by previous MOD are fabricated. The average functional cantilever beams are increased from 82 to 97, that is 12.47%. The increasement of functional devices is due to the reduction of stress and cracking.

As shown in Fig. 5, HP 4194 A Impedance/Gain Phase Analyzer has been used to test the mechanical resonance of the piezoelectric cantilever beam. This testing can be integrated electrically with the cantilever beams using standard CMOS processing. From Fig. 5, the first order of resonance frequency is about 240 kHz. If the piezoelectric cantilever beam works under the resonance frequency, the amplitude of beam deflection will be the maximum. Under this circumstance, the piezoelectric cantilever beam can work as a resonant sensor or a resonant actuator. If the piezoelectric cantilever beam works as a static actuator or sensor, the frequency of driving signal or the working frequency of the sensing system should be far bellow the resonance frequency.

4
Conclusions

In summary, PZT thin films have been formed on Pt/Ti/SiO_2/Si (1 0 0) substrates and Pt/Ti/LTO/Si_3N_4 cantilever beams by modified MOD method and then annealed at 700 °C in air for 1 h. The coating temperatures are controlled continuously rather than discontinuously to reduce the stress and cracking inside the PZT thin films. According to the experiments, the properties of PZT thin films are improved, the stress and cracking are reduced, and the functional devices under the other same situations are increased. A 0.5 μm PZT thin film has dielectric permittivity of 1698, remanent polarization of 13.66 $\mu C/cm^2$, and coercive field of 44.5 kV/cm. The deposition temperature dependence on thin film stress is investigated in the MOD PZT thin film. When continuously controlling the deposition temperatures, the stress of PZT thin film is reduced from 0.313×10^8 to 0.269×10^8 N/m, that is a change of 16.4%. Consequently, the number of functional

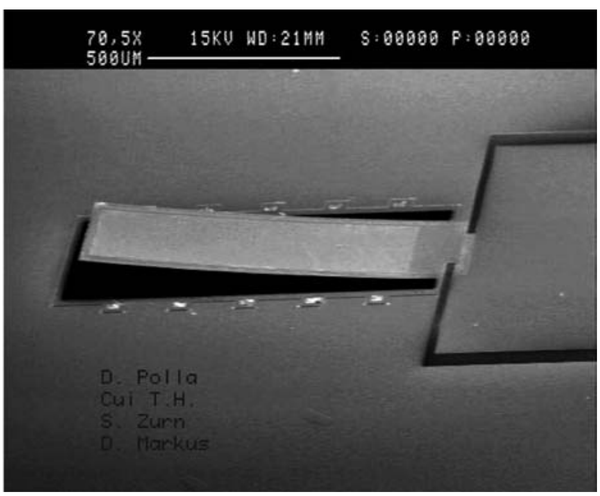

Fig. 4. SEM picture of a cantilever beam with MOD PZT thin films

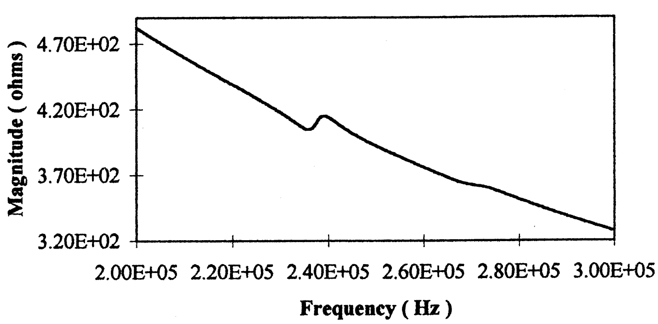

Fig. 5. Impedance magnitude measurement

devices is increased from 82 to 97, that is a change of 12.47%. The continuous controlling of the casting and annealing temperatures of the modified MOD method is very effective in aiding the improvement for PZT thin films' applications to microsensors and microactuators.

References

1. **Muralt P; Kohli M; Maeder T; Kholkin A; Brooks K; Setter N; Luthier R** (1995) "Fabrication and characterization of PZT thin-film vibrators for Micromotors" Sens. Actuators A 48: 157
2. **Scott JF; Paz de Araujo CA** (1989) "Ferroelectric memories". Sci 246: 1400
3. **Polla DL; Ye C; Tamagawa T** (1991) Surface-micromachined $PbTiO_3$ pyroelectric detectors. Appl Phys Lett 59: 3539
4. **Polla DL; Francis LF** (1996) Ferroelectric Thin Films in Microelectromechanical Systems Applications. MRS Bulletin, p. 59
5. **Lginbuhl P; Racine GA; Lerch P; Romanowicz B; Brooks KG; deRooij NF; Ranaud P; Setter N** (1995) Piezoelectric cantilever beams actuated by PZT Sol–Gel thin film. 8th International Conference on Solid State Sensors and Actuators, p. 413
6. **Udayakumar KR; Bart SF; Flynn AM; Chen J; Tavrow LS; Cross LE; Brooks R; Ehrlich DJ** (1991) "Ferroelectric thin film ultrasonic micromotors". Proceedings of IEEE Microelectromechanical Systems Workshop, pp. 109–113
7. **Ohba Y; Miyauchi M; Tsurumi T; Daimon M** (1993) "Analysis of Bending Displacement of Lead Zirconate Titanate thin film synthesized by hydrothermal Method". Jpn. J Appl Phys 32: 4095
8. **Koch M; Evans AGR; Brunnschweiler A** (1998) J Micromech Microeng 8: 119
9. **Vasant Kumar CVR; Sayer M; Passual R; Amm DT; Wu Z; Swanson DM** (1991) Lead Zirconate Titanate films by rapid thermal processing. Appl Phys Lett 58: 1161
10. **Davis AM; Gower MC** (1989) Epitaxial growth of thin films of $BaTiO_3$ using excimer laser ablation. Appl Phys Lett 55: 112
11. **Oikawa M; Toda K** (1976) Preperation of $Pb(Zr, Ti)O_3$ thin films by an electron beam evaporation technique. Appl Phys Lett 29: 491
12. **Castellano RN; Feinstein CG** (1979) Ion-beam deposition of thin films of ferroelectric Lead Zirconate Titanate (PZT). J Appl Phys 50: 4406
13. **Sakashita Y; Ono T; Segawa H; Tominaga K; Okada M** (1991) Preparation and electrical properties of MOCVD-deposited PZT thin films. J Appl Phys 69: 8352
14. **Peng CH; Desu SB** (1992) Low-temperature metalorganic chemical vapor deposition of perovskite $Pb(Zr_XTi_{1-X})O_3$ thin films. Appl Phys Lett 61: 16
15. **Zhu W; Vest RW** (1992) "Metallo-organic decomposition technology for PZT films in memory applications". Journal of Materials Proceeding Technology 29: 373
16. **Lee SS; White RM** (1998) Piezoelectric cantilever acoustic transducer. J Micromech Microeng 8(3): 230–238
17. **Lee SS; White RM** (1998) Piezoelectric cantilever voltage-to-frequency converter. Sensors and Actuators A71: 153–157