COMPOSITION DEPENDENCE OF MECHANICAL AND PIEZOELECTRIC PROPERTIES OF PULSED LASER DEPOSITED $Pb(Zr,Ti)O_3$ THIN FILMS

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***Abstract* — In this contribution we present the compositional dependence of the longitudinal piezoelectric coefficient ($d_{33,f}$), residual stress and Young's modulus of $Pb(Zr_x,Ti_{1-x})O_3$ (PZT) thin films. Pulsed laser deposition (PLD) was used to deposit epitaxial PZT thin films with a $< 110 >$ preferred orientation on silicon cantilevers. By using PLD, excellent piezoelectric properties of the PZT were observed which makes it an exciting piezoelectric material for the development of actuators and highly sensitive sensors. Our investigation of the compositional distribution of the piezoelectric coefficient ($d_{33,f}$) for 250 nm thick films shows a maximum value of 93 pm/V for x=0.52. The static deflection of the cantilevers, measured after the deposition of PZT thin films was used to determine the residual stress for various compositions. The observed trend in the residual stress of PZT thin films is attributed to the varying coefficient of thermal expansion for different compositions. The Young's modulus of the PZT thin films was determined by measuring the flexural resonance frequency of the cantilevers both before and after the deposition. The Young's modulus increases for the zirconium rich PZT compositions, which is in agreement with the trend observed in their bulk ceramic counterparts.**

***Keywords:* Cantilevers, residual stress, resonance frequency, Young's modulus, $d_{33,f}$, PZT, PLD.**

I – Introduction

The need for highly sensitive sensors and powerful actuators led the micro electromechanical systems (MEMS) industry to explore different materials in the micro- and nano domains. Excellent piezoelectric and ferroelectric properties of $Pb(Zr_x,Ti_{1-x})O_3$ (PZT) thin films makes it an extremely interesting material for the MEMS community [1]. To make PZT suitable for different types of applications, the composition of this material can be controlled by changing the Zr/Ti ratio [2]. To do so, a better understanding of the piezoelectric as well as the mechanical behaviour of PZT thin films of various compositions is needed. Recently, excellent ferroelectric properties have been obtained by using PZT deposited by pulsed laser deposition (PLD) [3]. The compositional dependence of the piezoelectric and mechanical properties of such PLD-PZT thin films is investigated experimentally in this work. To this end, micrometer sized measurement devices are employed. Our investigation focuses on three properties. Youngs modulus of PZT was determined accurately by using the shift in measured resonance frequencies of micro cantilevers [4, 5]. Deflections of the cantilevers as shown in Figure 1 were used to determine the residual stress in the PZT thin films. Piezoelectric coefficient ($d_{33,f}$) was determined by using PZT thin film capacitors, see Figure 2.

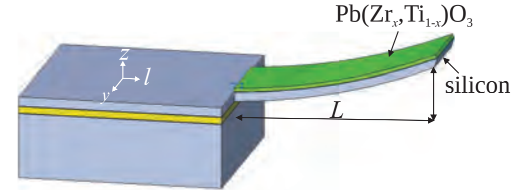

Figure 1: *Schematical representation of a cantilever fabricated from a silicon on insulator wafers. The upward static deflection is due to the tensile residual stress in the PZT thin film that was deposited on the cantilever.*

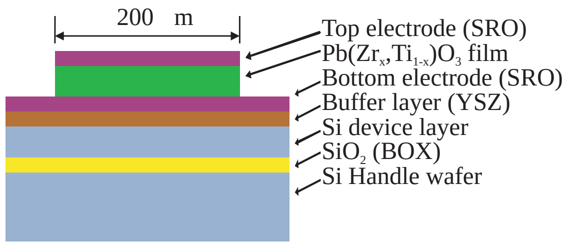

Figure 2: *Illustration of a PZT thin film between top and bottom electrodes. PZT capacitors are needed to measure the longitudinal piezoelectric coefficient. The thickness of the PZT film is 250 nm. The thickness of both the SRO electrodes and YSZ is 100 nm each.*

II – Fabrication

A dedicated SOI/MEMS fabrication process was used to fabricate 3 μm thick silicon cantilevers. The length of these cantilevers varies from 250 μm to 350 μm in steps of 10 μm with a fixed width of 30 μm. Deep reactive ion etching (DRIE) was used to etch the cantilevers on the device layer of (001) single crystal silicon on insulator wafers and to release the cantilevers from the handle wafer. The buried oxide was etched by using vapours of hydrofluoric acid. The released cantilevers were inspected and characterized by scanning electron and optical microscopy, see Figure 3.

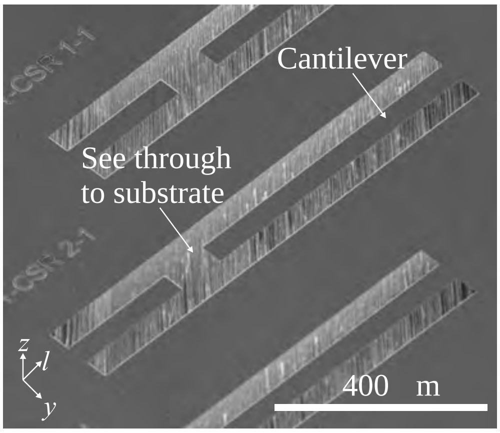

Figure 3: *Scanning electron micrograph of the fabricated cantilevers. Cantilevers were fabricated from a 3 μm thick silicon device layer. Length varies from 250 μm to 350 μm in steps of 10 μm with a constant width of 30 μm.*

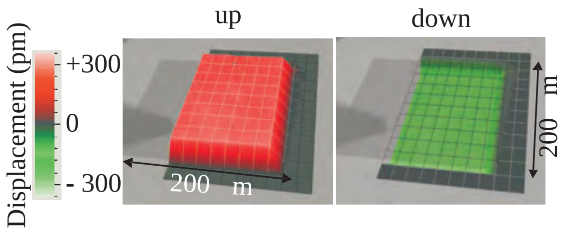

Figure 4: *Scanning laser-Doppler vibrometer measurements of a 250 nm thick $PbZr_{0.52}Ti_{0.48}O_3$ film. By applying an 8 kHz and 6 V peak to peak ac-voltage and measuring the maximum displacement of the top electrode, the piezoelectric coefficient ($d_{33,f}$) was measured.*

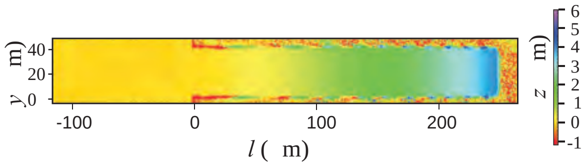

Figure 5: *White light interferometry measurements of the static deflection of a 250 μm long cantilever after deposition of the $PbZr_{0.52}Ti_{0.48}O_3$ thin film. Length and width of the cantilever are represented by l and y. Parameter z represents the transverse deflection of the cantilever.*

PLD was used to deposit 10 nm thick buffer layers of yttria-stabilized zirconia (YSZ) and strontium ruthenate (SRO) and 100 nm thick PZT on fabricated cantilevers. For the piezoelectric coefficient ($d_{33,\mathrm{f}}$) measurements, capacitors with in-plane dimensions of 200x200 μm^2 were fabricated on silicon. Starting with the deposition of 100 nm thick buffer layers of YSZ and bottom electrodes of SRO, the 250 nm thick PZT films were deposited followed by the deposition of a 100 nm thick top electrodes of SRO. All these films were deposited using PLD. Different Zr/Ti compositions of $Pb(Zr_x,Ti_{1-x})O_3$ (x=0.2, 0.3, 0.4, 0.52, 0.6 and 0.8) were deposited on separate samples. These samples were then used to investigate the compositional dependence of the piezoelectric and mechanical properties of the PZT thin films.

III – Experimental Details

The orientation of the deposited PZT thin films was analyzed by θ-2θ x-ray diffraction (XRD) scans (XRD, Bruker D8 Discover) with a Cu Kα cathode in the BraggBrentano geometry. Two different types of samples, cantilevers and capacitors, were analyzed separately to determine the preferred orientation of the PZT thin films. X-ray diffraction measurements were performed for all the compositions of PZT thin films that were used in this study.

The piezoelectric coefficient ($d_{33,\mathrm{f}}$) was determined by measuring the piezoelectric displacement of the PZT thin film capacitors. This displacement was measured by a MSA-400 micro system analyzer scanning laser-Doppler vibrometer. An 8 kHz and 6V peak to peak ac-voltage was applied on the top and bottom electrodes. The voltage results in the displacement of the PZT thin film that was measured by the displacement of the top electrode. The 2D scan of the top electrode in Figure 4 shows the piezoelectric response of the 200x200 μm^2 $PbZr_{0.52}Ti_{0.48}O_3$ film with a thickness of 250 nm. The measurements were conducted for all compositions of the PZT using identical structures.

The residual stress in different compositions of the deposited PZT thin films were determined by measuring the static deflection of the cantilevers using white light interferometry of the MSA-400 micro system analyzer. The profile of the cantilevers that was measured before the deposition of the PZT thin films was straight. The white light interferometer measurement of the 250 μm long cantilever deposited with $PbZr_{0.52}Ti_{0.48}O_3$ is shown in Figure 5. From this measurement we obtained the maximum deflection of the free end of the cantilever as shown in Figure 6. This information was used to calculate the curvature of the cantilevers for residual stress determination using using Stoney's equation (1) [6].

$$\sigma_\mathrm{f} = \frac{1}{6}\frac{E_\mathrm{s} t_\mathrm{s}^2}{R t_\mathrm{f}}, \quad \text{with} \quad R = \frac{L^2}{2\xi} \quad , \qquad (1)$$

the symbols σ, E, t, L, R and ξ are the residual stress, Young's modulus, thickness, length, radius of curvature and deflection, respectively. Subscripts 's' and 'f' denote the silicon and PZT thin film.

To determine the Young's modulus of PZT thin films, the resonance frequency of the cantilevers was measured by using a MSA-400 micro system analyzer scanning laser-Doppler vibrometer. Due to the addition of the PZT thin film on the cantilevers, the resonance frequency was changed, as expected. Measurements of resonance frequencies were conducted both before and after the deposition of the PZT thin films for cantilevers of varying length and for different compositions.

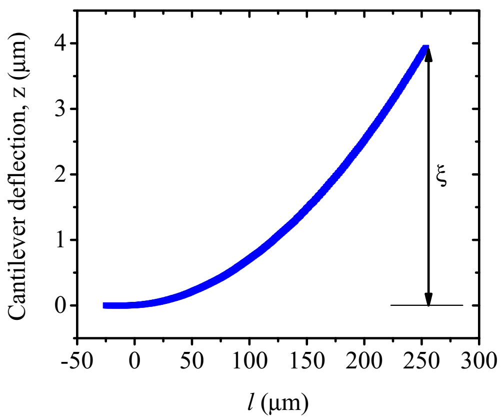

Figure 6: *Profile of the cantilever deflection after the deposition of PZT (x=0.52). A Maximum upward displacement ξ of the free end of the cantilever of almost 4 µm can be clearly seen from the image at l=250 µm.*

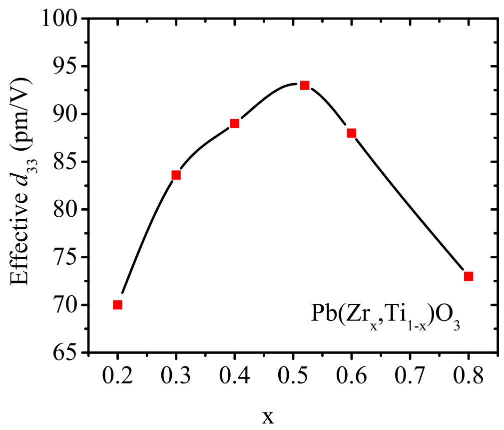

Figure 8: *The effective longitudinal piezoelectric coefficient ($d_{33,f}$) of different compositions. Based on our measurements we find the maximum value of $d_{33,f}$ for x=0.52. The lines are guides to the eye.*

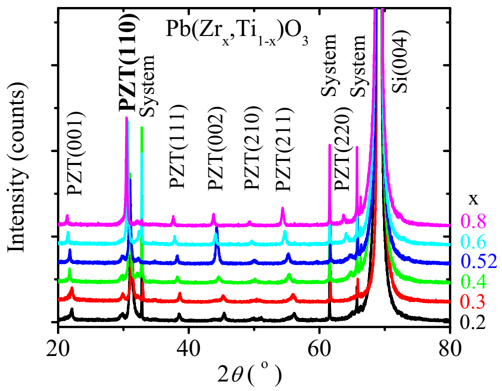

Figure 7: *Measured x-ray diffraction patterns of the pulsed laser deposited Pb(Zr$_x$,Ti$_{1-x}$)O$_3$ thin films, plotted for different compositions. The PZT films display a preferred (110) orientation.*

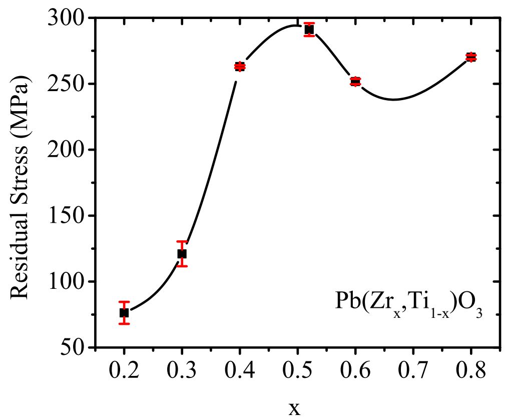

Figure 9: *Compositional distribution of the residual stress in the PZT thin films. Residual stress in the PZT thin film increases with the increasing Zr. content. The lines are guides to the eye.*

IV – Results and Discussion

The mechanical and piezoelectric properties of PZT thin films are dependent on film orientation. For instance, reference [7] discusses the dependence of the residual stress on film orientation. To confirm the orientation of our deposited PZT, we performed X-ray diffraction (XRD) measurements on samples of different compositions. Results reveal that PZT thin films grow with a (110) preferred orientation, see Figure 7.

Figure 8 shows the piezoelectric coefficient ($d_{33,\mathrm{f}}$) values for PZT thin films as a function of composition. Clearly, a strong dependence of the piezoelectric coefficient ($d_{33,\mathrm{f}}$) on the PZT composition is observed. This dependence shows the same trend as the bulk PZT ceramic counterparts [8]. In particular, the maximum value of piezoelectric coefficient ($d_{33,\mathrm{f}}$) of 93 pm/V was observed at x=0.52. This observation is in accordance with the piezoelectric response that is reported in literature for PZT thin films obtained by a sol-gel method [9]. We measured a high ($d_{33,\mathrm{f}}$) value of 123 pm/V at film thickness of 1 µm and x=0.52 composition, whereas 72 pm/V is reported for sol-gel PZT at that thickness [9].

The residual stress in PZT thin films of various compositions were found¡ to be tensile and strongly dependent on the film composition, as is shown in Figure 9. For Ti rich compositions of x=0.2 and 0.3, the value of residual stress is small compared to the Zr richer compositions of x=0.4 and above. The tensile residual stress in the PZT thin films increases upto x=0.52 with increasing zirconium content for our measured set of compositions. For x higher than 0.52 we find slightly reduced values for the residual stress. We suspect that this slight reduction may be related to the coefficient of thermal expansion of these compositions. For PZT ceramics, an increase in residual stress for increasing Zr content is attributed to an increase of the thermal expansion coefficient with increasing zirconium content [10]. The maximum value of the residual stress was found to be 291 MPa with a standard error of ± 5 MPa for

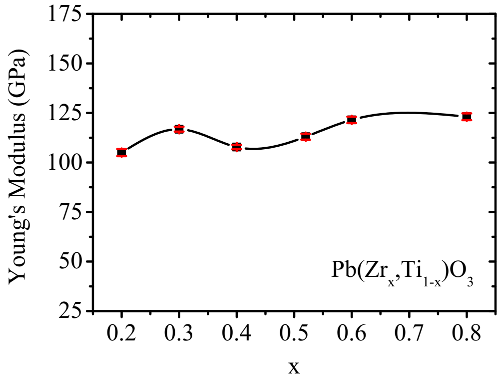

Figure 10: *Zr/Ti composition dependence of Young's modulus of the PZT thin films plotted as a function of Zr. content (x) in Pb(Zr_x,Ti_{1-x})O_3 thin films. The lines are guides to the eye.*

the PZT composition with the maximum piezoelectric coefficient ($d_{33,\mathrm{f}}$) (x=0.52).

The Young's moduli for PZT thin films with different compositions was determined and plotted in Figure 10. The Young's modulus value for the composition with the maximum $d_{33,\mathrm{f}}$ (x=0.52) was found to be 113.5 GPa with a standard error of $\pm$ 1.5 GPa. We observed an increase in the Young's modulus for the Zr rich composition, which is in agreement with published data for PZT ceramics [8].

V – Conclusions

We investigated the Zr/Ti composition dependence of the effective longitudinal piezoelectric coefficient ($d_{33,\mathrm{f}}$), the residual stress and the Young's modulus of Pb(Zr_x,Ti_{1-x})O_3 thin films. These PZT films were grown on micromachined silicon cantilevers using pulsed laser deposition. This process yields a (110) preferred orientation for all compositions studied in this work.

Compositional distribution measurements of the piezoelectric coefficient ($d_{33,\mathrm{f}}$) shows that the maximum value of $d_{33,\mathrm{f}}$ was observed at a composition of x=0.52. Compared to sol-gel, our PLD deposited PZT has a 70% higher $d_{33,\mathrm{f}}$ value at equal film thickness.

We studied the effect of the Zr/Ti composition on the residual stress of PZT, which was found to be tensile for all the measured Zr/Ti compositions. A maximum residual stress of 291 MPa with a standard error of $\pm$ 5 MPa was measured for the Pb($Zr_{0.52}$,$Ti_{0.48}$)O_3 thin film. The tensile residual stress in the films increases with increasing zirconium content.

The Young's modulus of film with different compositions was determined. The Young's modulus for the composition with maximum $d_{33,\mathrm{f}}$ (x=0.52) was found to be 113.5 GPa with a standard error of $\pm$ 1.5 GPa. We observed an increase in the Young's modulus value for the Zr rich composition which is in agreement with the published data for the PZT ceramic [8].

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