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High-rate sputtering of thick PZT thin films for MEMS

Harald Jacobsen · Klaus Prume · Bernhard Wagner · Kai Ortner · Thomas Jung

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Abstract Crack and void free polycrystalline Lead Zirconate Titanate (PZT) thin films in the range of 5 μm to 10 μm have been successfully deposited on silicon substrates using a novel high rate sputtering process. The sputtered PZT layers show a high dielectric constant ε_r between 1,000 and 1,800 with a moderate dissipation factor tan (δ) = 0,002−0,01 measured at f = 1 kHz, a distinct ferroelectric hysteresis loop with a remanent polarisation of 17 μC/cm^2 and coercive field strength of 5.4 kV/mm. The piezoelectric coefficients $d_{33,f}$ = 80 pm/V are measured by using a Double Beam Laser Interferometer (DBLI). Based on this deposition process a membrane actuator mainly consisting of a SOI layer and a sputtered PZT thin film was prepared. The deflection of this membrane actuator depending on the driving voltage was measured with a white light interferometer and compared to the results of **f**inite **e**lement **a**nalysis (FEA). With this approach a transverse piezoelectric coefficient of about e_{31}=−11.2 C/m^2 was calculated, whereas all the other material parameters in the model were lent from PZT-5A.

H. Jacobsen (✉)
Materials Science, Faculty of Engineering, University of Kiel,
Kiel, Germany
e-mail: harald.jacobsen@basf.com

B. Wagner
Fraunhofer Institute for Silicon Technology ISIT,
Itzehoe, Germany

K. Ortner · T. Jung
Fraunhofer Institute for Surface Engineering and Thin Films IST,
Braunschweig, Germany

K. Prume
aixACCT Systems GmbH,
Aachen, Germany

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1 Introduction

The large electromechanical coupling coefficient of PZT allows the realisation of actuators at high frequencies and low energy consumption. However, some designs, especially MEMS actuators for micro fluidic applications, require high quality PZT films with a thickness in the order of 10 μm.

Despite the fact that the deposition of PZT thin films is a field of intensive research, the fabrication of thicker films is still quite challenging. Although PZT thick films can be screen printed [1], a firing temperature above 900°C is necessary to achieve void free films and due to chemical reactions of evaporated lead, the silicon substrate can be damaged. Other common deposition techniques like MOCVD [2], magnetron sputtering [3] and Sol-Gel [4] suffer from low deposition rates and therefore are typically applied for the deposition of layers in micron range.

This work presents a high rate sputter process for the deposition of PZT films with a thickness of 5 μm up to 10 μm. As a first demonstrator a membrane actuator has been fabricated in a MEMS process flow and characterized.

2 Experimental

2.1 Gas flow sputtering

Gas Flow Sputtering is a special **p**hysical **v**apour **d**eposition (PVD) technique, based on a hollow cathode glow discharge and a gas flow driven material transport. Due to the hollow cathode effect a high power density can be

realised, resulting in a high plasma density and an intense sputter erosion of the target.

An argon flow through the cylindrical sputter source transports the eroded metal atoms to the substrate surface where the oxygen is added separately. All process gases are supplied by mass flow controllers.

For the deposition of the PZT films pure metallic targets were simultaneously sputtered. The working pressure of 0.5 mbar inside the vacuum chamber for the hollow cathode discharge was maintained by a roots blower unit and a vacuum rotary pump. The gas flow sputter technique is described in detail elsewhere [5, 6].

Since the gas flow sputter source has a limited diameter of 40 mm the substrate holder must be moved linearly to increase the coated area and to ensure the deposition of a uniform PZT film onto the wafer. During sputtering, the substrates are mounted on a heated wafer holder (chuck), where a bias-voltage is applied. The wafer holder allows substrate temperatures of up to 700°C during sputtering.

In order to obtain the desired crystallographic microstructure of the PZT films, the deposition temperature is of major importance. Experiments showed that a minimum temperature of 550°C is necessary to initiate a crystalline growth of the PZT film, while temperatures of approx. 620°C are required for the deposition of PZT films with good piezoelectric properties. Typical process parameters are summarised in Table 1.

2.2 Chemical composition

A crucial aspect which is essential for the presence of piezoelectricity is a distinct crystallinity. Larger grains and therefore the corresponding smaller number of grain-boundaries lead to smaller electrical losses. Intensive research concerning the microstructure, the grain size, and the growth behaviour of the polycrystalline PZT-films, has been performed and reported elsewhere [7]. Results show, that the main parameters regarding the grain size are the substrate temperature and the bias-voltage.

Another not less important aspect which can be discussed separately from the crystallinity is the stability and reproducibility of the chemical composition of the deposited thin films. Since the piezoelectric properties of PZT films depend strongly on their stoichiometry the repeatability of the composition within the process and from process to process becomes even more important.

Due to the lack of a vacuum load lock the wafers cannot be handled without breaking the vacuum. In other words, the target is exposed to the air with each new substrate. This leads to undefined conditions of the target, which induces different stoichiometries of the PZT-layers. Different approaches to overcome this problem are possible: upgrade the sputter system by a load lock, perform a source pre-conditioning after each substrate change, or by controlling the stoichiometry in-situ.

While the chemical composition of the deposited thin films can be measured using an **e**lectron **p**robe **m**icro **a**nalysis (EPMA) a more efficient way for in-line controlling is required. Analysing the plasma light emitted during sputtering by an **o**ptical **e**mission **s**pectroscopy (OES) unit, allows the measurement of the qualitative composition of the sputter plasma.

The emission spectrums are measured by a grating spectrometer (ARC, FC 45 91 80) with CCD-Detector. The intensity of the emission lines of Zirconium was found to be too small compared to the background signal. Thus, only the relative intensities of the emission lines of titanium and lead were used for determining the ratio of lead vs. titanium in the plasma.

Applying this approach, the key question is the degree of correlation between the chemical composition of the Plasma and the stoichiometry of the PZT layers.

In an experiment several samples were sputtered at different process conditions (power level, Argon flow). The results of the OES measurements of the plasma composition during these deposition processes compared to EPMA (SX100, Cameca) stoichiometries of the thin films are shown in Fig. 1.

Despite of its simplicity this approach shows a very good correlation between the chemical compositions in the plasma and the thin films. Thus obviously OES can be used for improving the stability and reproducibility of the chemical composition. In future work this approach will be pursued to control the stoichiometry of PZT-layers. A promising way could be to use the signal of the OES to adjust the power level of the sputter-source.

Table 1 Shows typical values of the process parameters.

Substrate temperature	550°C–650°C
Pressure	0.4 mbar–0.7 mbar
Argon flow rate	800 sccm
Oxygen flow rate	20 sccm
Source power	600 W
Source voltage	400 V–600 V
Bias AC voltage	50 V–100 V @ 200 kHz

3 Results and discussion

3.1 Material properties

The thickness of PZT films were determined by SEM (Fig. 2). Deposition rates of 200–250 nm/min were observed. These high sputter rates are about 20–25 times higher than reported from reactive magnetron sputtering [3] and demonstrate the potential of this sputter technique.

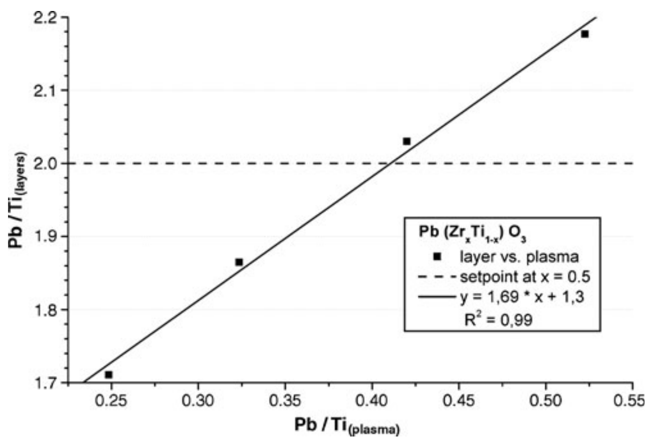

Fig. 1 The ratio of lead vs. titanium in the film (y-axis) is plotted against the ratio of lead vs. titanium in the plasma (x-axis). The target value for a layer with x=0.5 is achieved at a ratio of lead to titanium of 2 and is clarified by an additional dashed line. For these experiments, plasma power has been used as a parameter to influence both, plasma composition and layer stoichiometry

Typical layers had a thickness of 6 µm sputtered in about 30 min. However, even 16 µm thick PZT films were deposited without cracking or delamination within 90 min.

Electrical measurements of the relative permittivity ε_r have shown values between 1,000 and 1,800. A distinct ferroelectric hysteresis loop with a remanent polarisation of 17 µC/cm^2 and a coercive field strength of 5.4 kV/mm has been observed which is comparable to those of screen printed PZT [5]. Measurements of the piezoelectric coefficient $d_{33,f}$ using a DBLI [8] have shown values of the reverse effect of up to 79.7 pm/V.

3.2 Membrane actuator

To demonstrate the functionality of the PZT films, a membrane actuator was fabricated with a silicon based process flow. The membrane actuator consists mainly of the active, piezoelectric PZT film and the elastic silicon layer using an SOI layer. The membrane has a quadratic shape with a side length of about 2 mm.

This lateral dimension results in relatively large centre deflections of the membranes allowing the use of a commercial white-light interferometer (ATOS Micromap) to measure the bending of the actuated membrane.

The quadratic shape of the membrane is caused by the use of an anisotropic wet etchant (KOH solution, 30%, 80°C) during the membrane etching process. The principle design of the membrane is summarised in Fig. 3.

3.3 Process flow

150 mm SOI-Wafers with a SOI-(**s**ilicon-**o**n-**i**nsulators) thickness of about 20 µm and an overall thickness of about 675 µm are used as substrates. In a first process step a diffusion barrier of 500 nm thermal oxide, 150 nm Si_3N_4 and 100 nm **H**igh **T**emperature **O**xide (HTO, SiO_2) is deposited in a **l**ow-**p**ressure **c**hemical **v**apour **d**eposition (LPCVD) process. Because of its small lattice mismatch to PZT and its inert behaviour platinum is used as bottom electrode. To improve the adhesion of platinum it is recommended [9] to use titanium as adhesion layer. Both thin films were deposited by e-beam evaporation (Unaxis BAK). To improve the texture of the platinum layer the wafers are annealed at 550°C in a vacuum oven for 30 min at a pressure of less than 0.1 Pa. This process leads to a complete (111) texture of the platinum.

Afterwards, these wafers are sputter coated with a PZT thin film of approx. 4–5 µm thickness [5]. For structuring the PZT thin film a wet chemical etching mixture consisting of HCl and HF is used [10]. Tests ended up with an etch rate of the PZT between 1.3 µm/min and 1.6 µm/min leading to a total process time of approx. 4–5 min. Due to the HF content and the required etching time the photoresist shows strong delamination effects leading to a poor quality in transferring the pattern into the PZT layer. Thus in further experiments the photo resist is replaced by **p**lasma **e**nhanced **c**hemical **v**apour **d**eposition (PECVD) silicon nitride hard mask which was previously patterned in a dry etching process. The good adhesion of the Si_3N_4 hard mask on top of the PZT allows an almost perfect isotropic etching

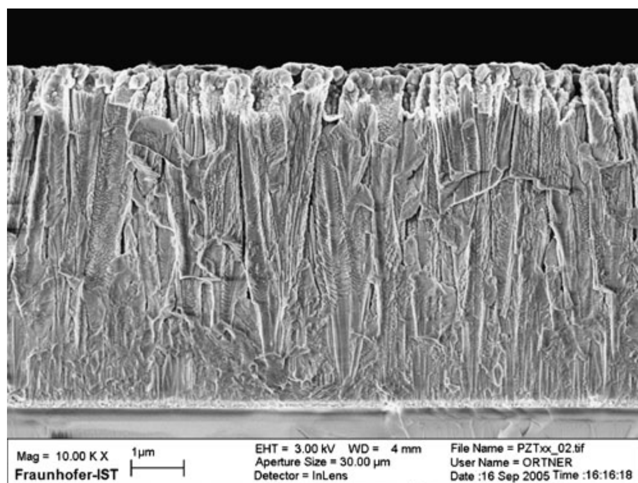

Fig. 2 SEM cross section of a 6.6 µm thick PZT film

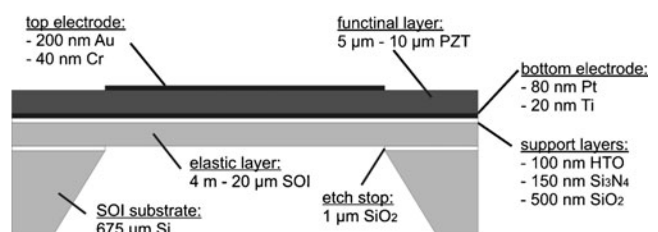

Fig. 3 Schematic view of the unimorph membrane actuator

of the PZT and leads to a drastically reduction in the under etching of the PZT layer to approx. 5 μm, see Fig. 4.

Finally the remaining silicon nitride layer is removed by dry etching. Subsequently a top layer is formed by local electroplating of gold with a thickness of 1.8 μm on a plating base consisting of 40 nm chromium and 200 nm gold. After removing the plating base the silicon nitride passivation on the rear side of the wafer is patterned by dry etching. This silicon nitride layer acts as hard mask during the deep anisotropic wet etching in KOH solution (Fig. 5). Finally the silicon oxide beneath the SOI layer is removed in a HF vapour etch process.

3.4 Membrane measurements and simulation

Poling of the test samples was carried out at 100°C with a field strength of 12.5 kV/mm for 30 min.. The centre deflection of the membranes is measured using a white-light interferometer.

Besides measurements the deflection of the membrane is also calculated in a FEA model using ANSYS assuming a transverse piezoelectric coefficient e_{31} of $e_{31} = -11.2$ C/m^2. The calculated values of the centre deflection and the measured ones are compared in Fig. 6.

Directly after the preparation the membranes of the test samples showed an initial curvature up to 0.5–1 μm which is very likely stress induced. Obviously the sputter process of the PZT film generates mechanical stress in the PZT layer in the range of approx. 40 MPa. Besides this pre-deflection of the membranes the tests showed variations in their responds on the actuation voltage and also a non-linearity in the voltage dependency of the deflections.

While the variations in the inclination of the measured curves can be attributed to small stoichiometry variations of the PZT compositions of the different samples the observed non-linearity can be either caused by stress stiffening of the membranes or due to a non-linear characteristics of the PZT material itself.

Currently the reason for this non-linear behaviour cannot be fully explained and further experiments and non-linear FEA are required to identify the causes for this phenomenon.

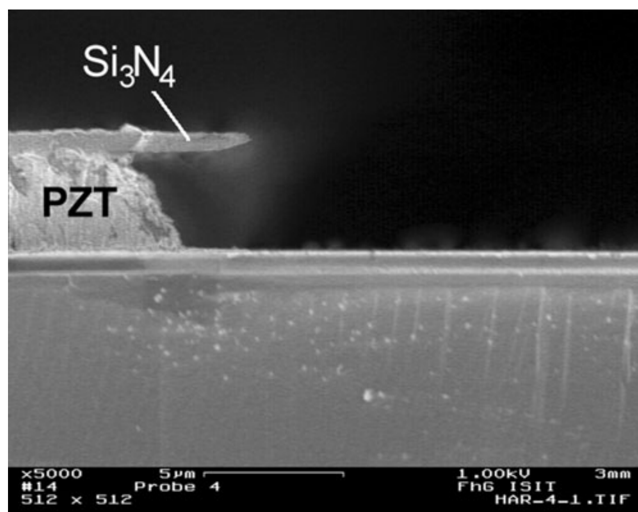

Fig. 4 SEM cross section of a 5 μm thick PZT layer etched by isotropic wet etching using a Si_3N_4 hard mask

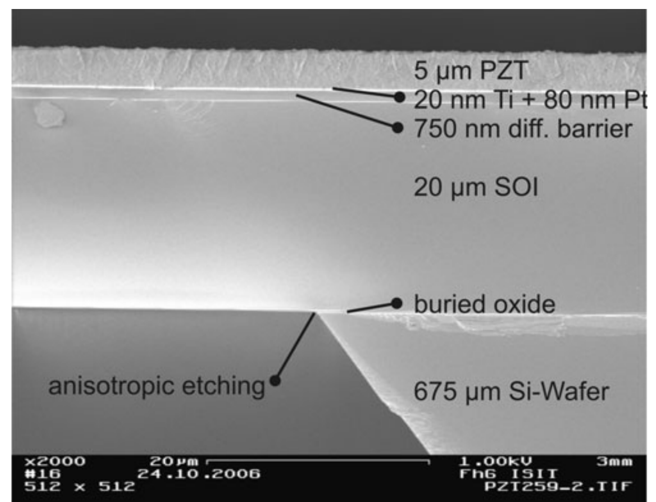

Fig. 5 SEM cross section of a corner of a membrane

4 Conclusion

Crack and void free polycrystalline PZT thin films in the range of 5 μm to 10 μm have been successfully deposited on silicon substrates using a novel high rate

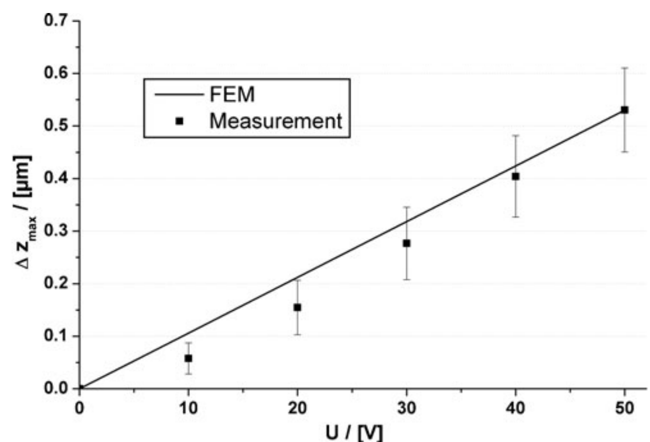

Fig. 6 Deflection of square shaped membranes: ■ measured results from eight membranes and—FEM results. For the linear FEA model a piezoelectric module e_{31} of −11.2 C/m^2 is assumed. The deviation between FEM (linear behaviour) and measurements might be related to electrostriction

sputtering process. With this sputter process sputter rates of 200–250 nm/min were achieved and complete 6″ wafers have been covered with a 12 μm thick PZT film within 60 min.

The PZT layers show a high dielectric constant ε_r between 1,000 and 1,800 with a moderate dissipation factor tan (δ) = 0,002−0,01 measured at f = 1 kHz, a distinct ferroelectric hysteresis with a remanent polarisation of 17 μC/cm^2 and a coercive field strength of 5.4 kV/mm. Measurements of the piezoelectric coefficient $d_{33,f}$ have shown values of the reverse effect up to 79,7 pm/V.

Based on this new deposition process a simple membrane actuator consisting of a SOI and a sputtered PZT layer was prepared. The deflection of this membrane actuator depending on the driving voltage was measured with a white light interferometer and compared to the results of a FEA model. With this approach a transverse piezoelectric coefficient $e_{31} = -11$ C/m^2 was calculated.

Still in an early stage of work the Gas Flow Sputtering approach for high rate deposition of PZT thin films has shown its high potential for application in MEMS actuators. Future work will concentrate on the optimisation and stabilisation of the PZT deposition process and to increase the piezoelectric coefficient $d_{33,f}$ and $d_{31,f}$ respectively.

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