In-situ large scale deposition of PZT films by RF magnetron sputtering

1. Introduction

Sputter techniques (PVD) are particularly suitable methods to grow PZT films. Both RF magnetron sputtering from a single ceramic target [1,2] and DC magnetron sputtering from multiple targets [3,4] are methods capable to deposit films with a high quality. As a remarkable advantage compared to competing chemical [5-8] deposition methods the PVD deposition method facilitates the in-situ growth of PZT films without additional post annealing step. Further on since sputter techniques are already applied in thin film industry for a long time they are as well very competitive for cost sensitive volume production of PZT films.

One prerequisite for the in-situ growth of the correct crystalline perovskite structure is the tight temperature control of the substrate in the range of 500°C during film deposition. Challenges arise because of the required temperature uniformity especially for the large wafer size of 200mm. Further on the sputter equipment has to be optimized to enable a deposition process at a high throughput which is a key factor for minimized cost of ownership for PZT volume production.

In the present study high quality PZT films were deposited by RF magnetron sputtering onto platinum electrodes on top of 200mm oxidized silicon wafers at deposition temperatures (T_{dep}) between 550°C – 700°C.

The sputtering was from a single ceramic PZT target with an appropriate excess of PbO. Further on the platinum electrodes were covered with a thin TiO_2 seed layer to promote the perovskite nucleation process [9, 10].

As the result the high substrate temperatures allowed the direct growth of the piezoelectric perovskite phase and therefore renders the additional post annealing step unnecessary. Structural, compositional and electrical characterization were performed to analyze the crystalline structure, film stoichiometry and the dielectric, ferroelectric and piezoelectric properties.

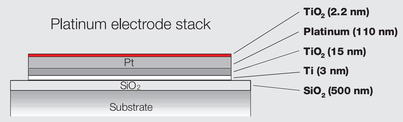
2. Experimental

Platinum electrodes were grown by sputter deposition onto 200mm oxidized silicon wafers. Intermediate Titanium and TiO_2 films serve as adhesion and barrier layer respectively. Finally a very thin TiO_2 seed layer was sputtered on top of the Platinum.

The thicknesses of all layers were controlled by XRR and XRD measurements showed evidence for a (111) preferential crystallographic orientation of the Pt film with minor contributions of (311) and (200) orientations. A post annealing treatment of the Platinum electrode prior to the PZT deposition was found to reduce the spurious peaks substantially.

The sputtering was from a 300 mm single ceramic target with an Zr/Ti ratio of 52/48 and a appropriate excess of PbO to compensate the lead loss due to evaporation at high process temperatures.

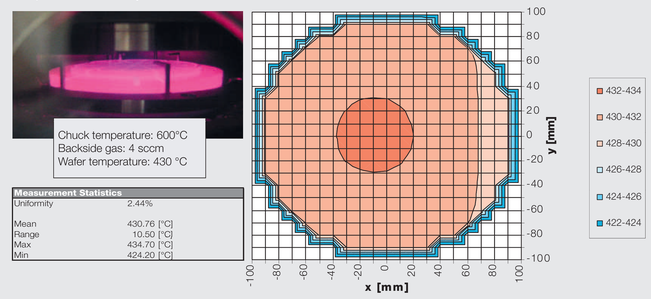
The PZT films of 1 µm thickness were sputtered in a pure Ar atmosphere at a process pressure of 2 mtorr. The sputter power was adjusted to reach a deposition rate higher than 40 nm/min



The PZT depositions were performed in a dedicated RF sputter module attached to an Oerlikon CLN 200 II sputter system. The main features of the RF sputter chamber are

- Heated substrate holder (chuck) which is capable to reach a maximum heater temperature of more than 750°C. This enables depositions at a substrate temperature up to ~ 650°C with a very good uniformity on 200mm wafers as measured with a silicon SensArray monitor wafer.
- Maximum RF sputter power of 5kW to enable high deposition rates
- Optimized gas distribution system for high plasma uniformity especially in reactive sputter mode with oxygen supply
- Facility to apply additional RF power to the substrate to influence the substrate potential (RF Bias)
- Phase locked synchronization of cathode and substrate RF power by master oscillator

Temperature uniformity of 8“ substrate holder



Temperature uniformity of a 8-inch substrate holder (chuck) at temperature set point 600°C. The data achieved with a silicon SensArray monitor wafer show an excellent temperature homogeneity which is necessary for in-situ sputter deposition of high quality PZT films.

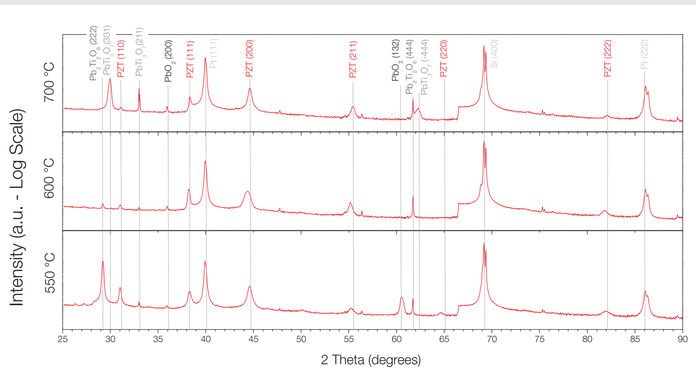
To identify the temperature range for in-situ growth of the perovskite phase the deposition temperature (T_{dep}) was varied between 550°C and 700°C. The film were characterized by means of

- XRD θ-2θ measurements to detect the phase formation and the preferential crystallograhic orientation
- Wavelength dispersive X-ray spectroscopy (WDS) to measure the film stoichiometry.

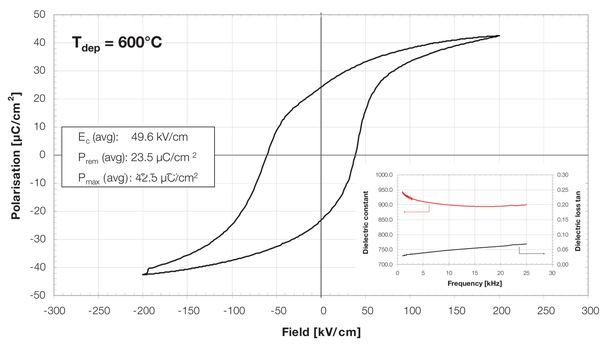
Finally from the films showing the best structural and compositional results device samples were structured for further electrical characterization.

- Hysteresis and small signal capacitance measurements
- Double Beam Laser Interferometry to determine $d_{33,f}$
- 4-Point Cantilever Bending Method to determine $e_{31,f}$

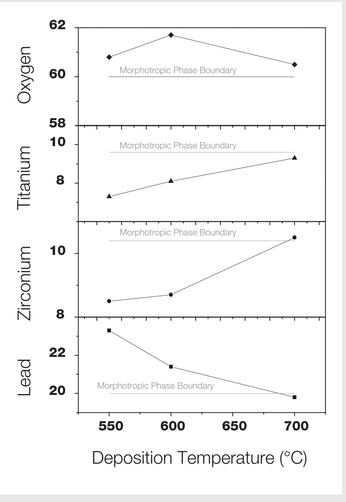
3. Results



XRD θ-2θ scan of PZT films deposited at different deposition temperatures. At an intermediate temperature of 600°C the PZT films crystallize mainly in the perovskite structure. At a lower temperature the excess of Pb results in spurious secondary phases ($Pb_2Ti_2O_6$ and PbO_2). At a higher temperature the Pb and oxygen deficient $PbTi_3O_7$ phase evolves in addition to the PZT perovskite structure [9].



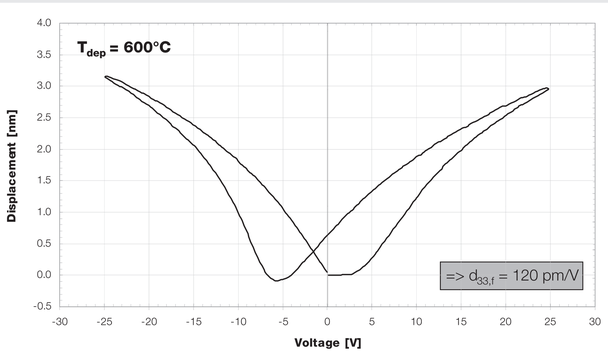
Ferroelectric hysteresis of films sputtered at 600°C deposition temperature. The small signal capacitance measurement (inset) show a dielectric constant ε = 947 and a dielectric loss tanδ = 3% at 1kHz.



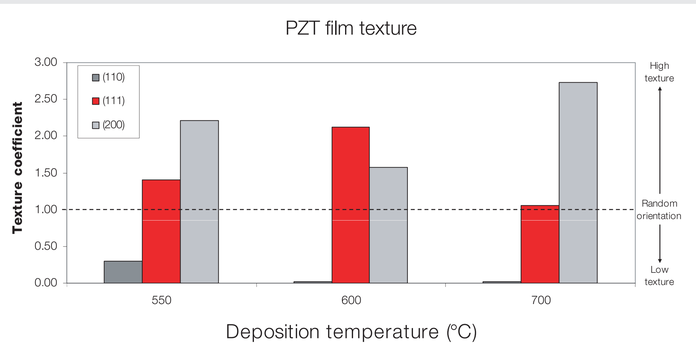
Evolution of PZT film stoichiometry as a function of deposition temperature by means of Wavelength Dispersive X-Ray Spectrocopy (WDS) at 10keV beam energy. The Pb concentration shows a clear downward trend as a function of substrate temperature, in contrast to the Ti and Zr concentration.The oxygen content remains almost stable.

Although at 700°C the film composition is very close to the morphotropic phase boundary stoichiometry with Pb/(Zr+Ti) ~ 1 and Zr/(Zr+Ti) ~ 0.53 the films at intermediate temperature of 600°C show the lowest amount of spurious secondary phases.
This can be understood taking into account the different penetration depth at the X-ray and electron beam excitation. At 10keV beam energy WDS is more surface sensitive compared to XRD θ-2θ scans which probe mainly the film volume.

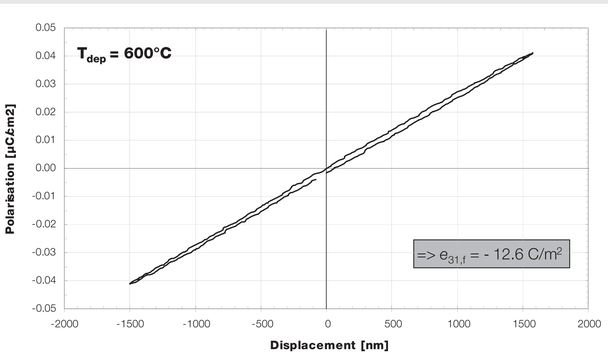
Therefore the mismatch between the best results from XRD and WDS analysis could be an indication for the existence of a temperature downward gradient towards the film surface. As the result the Pb concentration in the film volume is lower compared to the surface which is supported by the detection of a Pb deficient secondary phase in the films deposited at 700°C.



Measurement of piezoelectric coefficient $d_{33,f}$ of PZT films sputtered at 600°C deposition temperature by double beam laser interferometry (aixDBLI from aixACCT). The $d_{33,f}$ value of the sputtered film is comparable to the performance of state-of-the-art thin films deposited with a CSD process.



Evolution of PZT film texture as a function of deposition temperature. At lower and higher temperatures the grains crystallized in the perovskite phase show mainly a (200) orientation. In contrast the films deposited at 600°C with an almost pure perovskite structure contain a higher amount of (111) oriented grains. This behaviour can be expected for a functional TiO_2 seed layer at a thickness of a few nanometer which promotes the (111) preferred orientation of PZT growth [10].



Measurement of piezoelectric coefficient $e_{31,f}$ of PZT films sputtered at 600°C deposition temperature by 4-point cantilever bending method (aix4PB from aixACCT). The $e_{31,f}$ value is calculated from the measured polarisation and the strain of the sample during bending.

4. Conclusions

PZT layers were grown in-situ on 200 mm (111) oriented Pt bottom electrodes, which were covered by a thin TiO_2 seed layer.

As a consequence of the high deposition temperature (T_{dep}) the perovskite phase could be grown directly without any additional post annealing step.

The evolution of the Pb/(Zr+Ti) atomic ratio as a function of T_{dep} exhibits a downward trend, with the morphotropic phase boundary stoichiometric value Pb/(Zr+Ti) ~ 1 and Zr/(Zr+Ti) ~ 0.53 obtained at ~ 700°C.

However, the XRD patterns indicate that the films prepared at intermediate T_{dep} ~ 600°C exhibit the minimum volume fraction of the spurious pyrochlore phase, in addition to the tetragonal and rhombohedral piezoelectric PZT structures.

As a result the highest piezoelectric coefficients $d_{33,f}$ = 120 pm/V and $e_{31,f}$ = -12.6 C/m² were obtained for these films deposited at T_{dep} ~ 600°C.

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For more information about this cooperative project entitled “High volume piezoelectric thin film production process for microsystems” (piezoVolume) please see www.piezovolume.com

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