RF Magnetron Sputtering Deposition of PZT on Silicon Substrates
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INTRODUCTION
Ferroelectric thin films, especially lead zirconate titanate (PZT) thin film, have been intensively studied in recent years e.g. for applications in ferroelectric random access memory devices (FeRAM) [1], micro-electromechanical systems (MEMS) [2] and electro-optical devices [3]. For all these applications, the fundamental requirement is the growth of good quality films on specific substrates and/or electrode materials. Various techniques have been used to deposit PZT films, such as sputtering, sol-gel and metal-organic chemical vapour deposition. Among these sputtering is promising because of its simple process control. In general to obtain PZT films containing the ferroelectric perovskite phase as grown films need to be annealed between 500°C and 800°C. High temperature annealing poses several problems such as stress induced film cracking and element interdiffusion with the electrode/substrate. Moreover the role played by phase transformations, composition and morphology still need to be fully understood to optimize PZT thin film growth.

In the present investigation we report on our results on PZT films deposited on Si(100) substrates.

EXPERIMENTAL
PZT thin films have been deposited at room temperature by r.f. magnetron sputtering from a Pb1.2Zr0.52Ti0.48O3 target at 300 Watt RF power under a stream of 10 sccm Ar/5% O2 gas. Deposition duration was 2 hours and film thickness determined from profilometry was about 130 nm. Annealing at 650°C and 750°C for 10 min was carried out by inserting samples into a pre-heated muffle furnace. Grazing incidence X-ray diffraction (GIXRD) spectra were recorded at a beam incidence angle 2θ=4 deg using a Philips PW 3020 powder diffractometer with Ni filtered Cu Kα radiation. Composition measurements were carried out by Rutherford Backscattering Spectrometry (RBS) at the CN accelerator of INFN-LNL laboratories using 3.6 MeV 4He+ ions. Spectra were analyzed by using the RUMP simulation package to simulate the spectra and to determine element doses from peak integrals using the surface energy approximation. SEM imaging of the surface texture was performed with a FEI nova 600i dual beam system. All the SEM analyses have been carried out at 5 kV.

RESULTS AND DISCUSSION
The 3.6 MeV 4He+ RBS spectra for as deposited and annealed PZT films are shown in figure 1. Well separated steplike signals of Pb, Zr, Ti, O are visible. The determined PZT film stoichiometries are reported in Table 1. For the "as grown" film sizeable excesses of Pb and O with respect to the desired Pb(Zr0.52Ti0.48)O3 stoichiometry of perovskite PZT are observed that we attribute to the lead rich composition of the sputtering target as observed previously in the literature [4]. On the other hand the Zr:Ti ratio is close to the expected one. By annealing the Zr:Ti ratio approaches further the desired Zr:Ti=0.52:0.42 ratio because of Ti diffusion into the Si substrate, while the Pb excess decreases, even though it does not vanish. The O excess initially decreases upon annealing at 650°C, probably related with PbO evaporation, and then increases again by annealing at 750°C.

![RBS spectra of PZT films as grown and annealed on Si(100) substrates.](image)

In the spectra of figure 1 we observe a pronounced Pb diffusion into the Si substrate, evidenced by the formation of a strong shoulder at the lower energy side of the Pb step and a corresponding intensity decrease at the Si edge of the substrate. 

Table 1. PZT films stoichiometry determined from 3.6 MeV 4He+ RBS spectra. The element concentrations have been normalized so that Ti + Zr = 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pb</th>
<th>Zr</th>
<th>Ti</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>as grown</td>
<td>1.44±0.02</td>
<td>0.48±0.01</td>
<td>0.52±0.01</td>
<td>5.3±0.3</td>
</tr>
<tr>
<td>650°C</td>
<td>1.28±0.02</td>
<td>0.53±0.01</td>
<td>0.47±0.01</td>
<td>3.7±0.3</td>
</tr>
<tr>
<td>750°C</td>
<td>1.27±0.02</td>
<td>0.52±0.01</td>
<td>0.48±0.01</td>
<td>4.3±0.3</td>
</tr>
</tbody>
</table>
Also a widening and a decrease of the intensity of the O signal can be observed, indicating diffusion of O into the Si substrate. The excess of O at 750°C is probably related with the O diffused into the Si substrate while the film O content is replenished by the annealing atmosphere (air).

In figure 2 are shown the GIXRD spectra of PZT films before and after annealing. As grown PZT films contain a mixture of different lead oxides, including orthorhombic $\alpha$-PbO$_2$ scrutinite (full squares), hexagonal PbO$_{1.37}$ (full circles) and tetragonal PbO litharge (full triangles) as well as a cubic "pyroclore type" Pb$_2$(Zr,Ti)$_2$O$_6$ phase (open circles). The dominance of lead oxides in the as grown film appears reasonable in view of the measured large Pb and O excess. By annealing at 650°C for 10 min the lead oxide peaks disappear and only the pyroclore peaks remain. A shift of the pyroclore peaks to higher Bragg angles is observed with increasing annealing temperature similar to that observed previously in the literature for PbTi$_3$O$_7$ pyroclore [5]. In films annealed at 750°C in addition to pyroclore phase the perovskite PZT phases (open squares) develops. The perovskite peaks match well with rhombohedral perovskite but presence of additional tetragonal perovskite may not be excluded. For the tetragonal perovskite the $\{002\}$ peak should be splitted into two peaks located at $2\theta = 45,09^\circ$ and $2\theta = 43,71^\circ$.

A splitting is not observed but the $\{020\}$ peak is wider than the other peaks, suggesting the presence of some tetragonal perovskite. This agrees with the expectations based on the measured stoichiometry Zr,Ti=0.52:0.48 that matches exactly the composition of the morphotropic phase boundary. By comparing the relative peak intensities of XRD $\omega$-2$\theta$ scans with the tabulated ICCD-JCPDS powder diffraction intensities we conclude that the perovskite phase is slightly preferentially oriented with the $\{020\}$ planes parallel to the film surface.

SEM images of as-grown PZT films are shown in figure 3. The film surface is very smooth and exhibits a "globular" structure with 100 nm sized "globules". A closer inspection (Figure 3b) reveals that "globules" are internally structured by elongated nanosized grains having typical widths 9-11 nm and lengths 20-40 nm. This size range agrees well with the crystallite size obtained from XRD peak widths by using the Scherrer formula, that indicate a crystallite size of 9 nm for the pyrocrle phase. Since films annealed at 650°C are purely pyroclore films, we conclude that nanosized elongated grains are associated with the Pb$_2$(Zr,Ti)$_2$O$_6$ pyroclore phase. Similar elongated grains were correlated in Ref. [4] with a lead deficient PbTi$_3$O$_7$ pyroclore phase. In our case however pyrocrle films were not lead deficient as it is evident from the RBS composition data.

**CONCLUSIONS**

PZT films have been deposited on silicon substrates by RF-magnetron sputtering. As grown films show large lead and oxygen excesses and contain mainly lead oxides. The lead excess decreases with increasing annealing temperature - as expected - apparently through a combination of PbO evaporation and Pb diffusion into the Si substrate. Upon high temperature annealing at 750°C the films undergo a phase transformation into a mixture of pyrocrle Pb$_2$(Zr,Ti)$_2$O$_6+x$ and perovskite PZT phases. The pyrocrle phase was found to be associated with elongated nanometer sized grains.