

Compositional and Microstructural Study of Sol-Gel-Derived $PbZr_{0.3}Ti_{0.7}O_3/Al_2O_3/SiO_2/Si$ Thin-Film Structures

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Abstract: In this work we discuss the results of compositional and microstructural analyses of $PbZr_{0.3}Ti_{0.7}O_3/Al_2O_3/SiO_2/Si$ thin-film structures. The $PbZr_{0.3}Ti_{0.7}O_3$ (PZT) and Al_2O_3 thin films were prepared by the alkoxide-based sol-gel method. A dense, nanocrystalline, 20-nm-thick, γ -alumina layer was formed on the silicon substrate after annealing at 900°C for 1 hour. On top of this alumina layer, a PZT film with a <100> orientation of the tetragonal perovskite phase, about 300-nm-thick, was obtained after annealing at 550°C. The alumina layer did not completely prevent the diffusion of lead oxide from the PZT to the Si substrate. An additional Al-Si-Pb-O amorphous layer with a maximum thickness of 10 nm was observed between the Al_2O_3 and SiO_2 layers.

This work is dedicated to the late Professor Marija Kosec

Keywords: PZT thin films, interface reactions, SEM, TEM

Fazna in mikrostrukturna analiza tankoplastnih struktur $PbZr_{0.3}Ti_{0.7}O_3/Al_2O_3/SiO_2/Si$, pripravljenih s sol-gel sintezo

Izleček: V delu so predstavljeni rezultati fazne in mikrostrukturne analize tankoplastnih struktur $PbZr_{0.3}Ti_{0.7}O_3/Al_2O_3/SiO_2/Si$. Z alkoksidno sol-gel sintezo smo pripravili tanke plasti s sestavo $PbZr_{0.3}Ti_{0.7}O_3$ (PZT) in Al_2O_3 na silicijevi podlagi. Po segrevanju na 900°C, 1 uro smo uspeli pripraviti gosto, 20 nm tanko plast γ -aluminijevega oksida na silicijevi podlagi. Na površino omenjenega aluminijevega oksida smo nanесли 300 nm tanko plast PZT, ki ima po segrevanju pri 550°C tetragonalno simetrijo in je orientirana v smeri <100>. Tanek sloj aluminijevega oksida ni popolnoma preprečil difuzije svinčevega oksida iz PZT v silicijevo podlago. Med Al_2O_3 in SiO_2 smo opazili dodatno, 10 nm amorfno plast Al-Si-Pb-O.

Ključne besede: Tanke plasti PZT, reakcije med plastmi, SEM, TEM

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1 Introduction

A lead-zirconate-titanate solid solution, with a composition close to the morphotropic phase boundary, is used in many multilayered structures due to its outstanding piezoelectric and ferroelectric properties. However, in order to obtain a stronger piezoelectric response, interdigitated electrodes (IDEs) have been introduced to replace the traditional parallel-plate electrode configuration, for example in energy-harvesting applications. [1,2] However, an IDE system requires a direct contact between the active film and the substrate. The direct

integration of the piezoelectric $Pb(Zr,Ti)O_3$ layer on the silicon substrate leads to the formation of lead-silicate glass phases, which are not piezoelectric.[3] In order to prevent these undesired reactions, many materials were studied as barrier layers, such as Al_2O_3 [4,5,6], $Ba(Mg_{1/3}Ta_{2/3})O_3$ [7], $MgAl_2O_4$ [8] and Ir.[9]

Alumina is a very good candidate for this barrier layer due to its chemical and thermal stability. Thin alumina layers, as a barrier layer between the $Pb(Zr_{0.52}Ti_{0.48})O_3$ and Si substrate, were prepared by a sol-gel route [4], by chemical vapor deposition (CVD) [5,6] or by a com-

bination of the two, i.e., the sol-gel and the CVD methods.[10] Depending on the method used and the heat-treatment conditions, amorphous or crystalline alumina was obtained.[4,5,6] For example, a pure crystalline alumina layer was obtained after annealing at 750°C for 30 min using the sol-gel method[4], and at 1000°C using the CVD method.[5,6] In addition, by using the CVD method, <001> or <111> oriented alumina films can also be grown on the silicon.[5]

However, despite the fact that there are a number of articles about the influence of the alumina layer on the functional properties of $\text{Pb}(\text{Zr,Ti})\text{O}_3$ films, any detailed structural characterization of these multilayered thin-film structures is usually missing.

In this work we used the sol-gel route in order to prepare a $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3/\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ thin-film structure. The aim of the work was, first, to analyze the phase composition and the microstructure of the alumina layer and, second, to evaluate the chemical compatibility between the alumina and the $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3$ film. The analyses from the micro- to the nano-level were performed by X-ray diffraction and analytical microscopy methods.

2 Experimental

An alumina precursor solution with a concentration of 0.25 M was prepared in a dry atmosphere by dissolving aluminum sec-butoxide, $(\text{Al}(\text{O}-\text{secC}_4\text{H}_9)_3)$, Aldrich) in 2-methoxyethanol ($\text{CH}_3-\text{O}-\text{CH}_2-\text{CH}_2-\text{OH}$ (2-MOE), Alfa Aesar). The solution was then intensively stirred in a dry box for 1 hour.

A precursor solution with the composition $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3$ and 10% excess of PbO was prepared in an atmosphere of dry nitrogen by mixing dehydrated lead acetate ($\text{Pb}(\text{OAc})_2$, Alfa Aesar) titanium iso-propoxide ($\text{Ti}(\text{O}-i\text{C}_3\text{H}_7)_4$, Alfa Aesar) and zirconium iso-propoxide ($\text{Zr}(\text{O}-i\text{C}_3\text{H}_7)_4$, Alfa Aesar) in 2-MOE. After the mixing, the solution was refluxed for 2 hours and distilled to reach a concentration of ~0.5 M. After cooling to room temperature, 4 vol.% of formamide (HCONH_2 , Alfa Aesar) was added to the solution. A detailed description of the $\text{Pb}(\text{Zr,Ti})\text{O}_3$ solution's preparation can be found in.[11]

A thin alumina film was prepared by spin-coating (3000 rpm, 30 sec) the precursor solution on the SiO_2/Si substrate. Four layers of solution were deposited; after which each layer was dried for 5 min. at 200°C and given 5 min. of pyrolysis at 350°C. After the fourth layer, the thin-film $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ structure was annealed at 900°C for one hour with a heating rate of ~14°C/min.

Later, four layers of $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3$ solution were deposited on an $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ substrate (3000 rpm, 30 sec), with each deposition being followed by 2 min. of drying at 200°C and 2 min. of pyrolysis at 350°C. After the deposition of each second $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3$ layer (subsequently denoted as the PZT layer) the $\text{PZT}/\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ structure was exposed to rapid thermal annealing at 550°C for 15 min in air. The heat-treatment conditions were defined according to Malič et al.[12]

The thermal decomposition of the aluminum precursor solution, dried at 60°C, was followed by thermogravimetry and differential thermal analysis (TG/DTA, Netzsch STA 409), using a heating rate of 10°C/min. in a Pt crucible and an atmosphere of air.

The phases of the thin-film structures were determined with an X-Ray diffractometer (CuK α radiation, Philips PW 1710) in the range $2\theta=10^\circ-65^\circ$ using a step of 0.034° per 100 seconds.

Prior to the scanning electron microscope (SEM) and focused ion beam (FIB) microscope analyses the samples were coated with carbon in a sputter coater (SCD 050, BALTEC) to prevent charging and to provide electrical conductivity.

For the transmission electron microscopy (TEM) cross-section observations the thin-film samples were cut into pieces with a wire-saw, after which two pieces were glued together, head-to-head, with highly dispersed epoxy glue, and then glued into a copper ring. After the hardening of the glue, the thickness of the sample was mechanically reduced by grinding from 1 mm to ~100 μm . The sample was then dimpled from one side to a final thickness of ~20 μm . Finally, thin disks were exposed to an ion-milling procedure with 3.5-keV argon ions using a precision ion polishing system (PIPS, Gatan, Model 691). The areas adjacent to the specimen hole were used for the TEM observation.

The thin-film structures were characterized using a field-emission SEM (FE-SEM, Jeol JSM-7600F), a FIB microscope (FIB, Helios Nanolab 650, FEI) equipped with an INCA X-ray energy dispersive spectrometer (Oxford Instruments), a transmission analytical electron microscope (TEM, Jeol JEM-2100) and a high-resolution TEM (TEM, Jeol JEM-2010F) equipped with an Oxford LINK ISIS 300 energy-dispersive X-ray spectrometer (EDXS).

3 Results and discussion

3.1 Preparation and characterization of the alumina thin film on the SiO₂/Si substrate

In order to define the annealing conditions, a thermal analysis of the dried starting aluminum alkoxide solution was performed. The obtained TG and DTA curves are presented in Figure 1. During heating from room temperature to ~500°C the sample loses 50% of its mass, above 500°C no significant mass loss is observed. The mass loss is accompanied by an endothermic peak at ~140°C, which can be related to the evaporation of water and residual solvent, and the exothermic peak at ~310°C, which can be attributed to the decomposition of organic species.[13]

The DTA curve shows two additional exothermic peaks at ~870°C and ~1110°C.

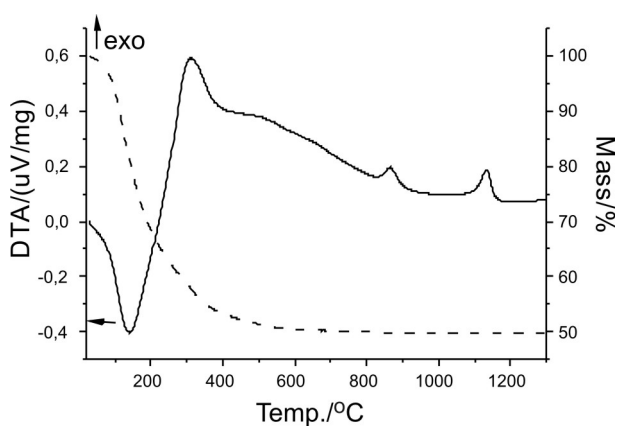
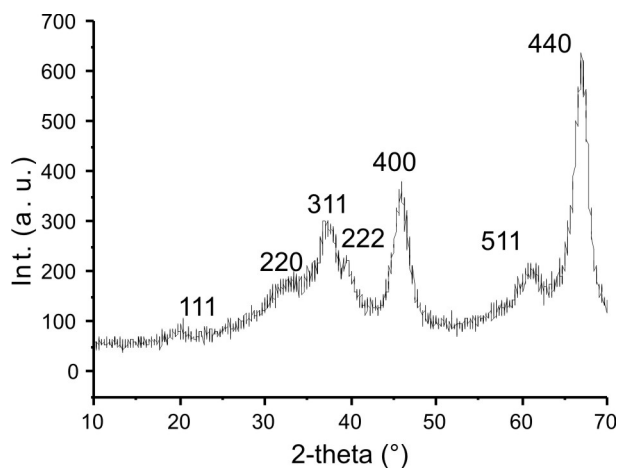


Figure 1: TG/DTA curves of aluminum alkoxide solution performed from 20°C to 1400°C.

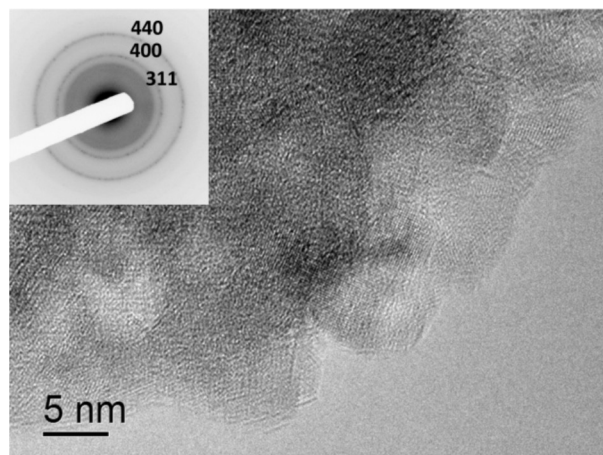
The exothermic peak at 870°C could be related to the crystallization of the cubic γ -alumina from the amorphous gel. According to Bahlawane et al.[14] the γ -alumina crystallizes in the 850-900°C temperature range when using aluminum alkoxide as a precursor. The exothermic peak at 1100°C could be related to the growth of the γ -alumina crystals, which is an exothermic process. However, let us note that at the same temperature, above 1100°C, the alumina also transforms to the rhombohedral α -alumina. Most probably in our case these two effects overlap.

Based on the TG/DTA analysis, the dried aluminum precursor was annealed at 900°C for 1 hour, and, in order to characterize the obtained powder, XRD and TEM analyses were performed. An XRD pattern and a TEM bright-field image are shown in Figure 2. Figure 2(a) shows that all the peaks in the XRD pattern can be indexed by γ -alumina with a defect cubic spinel structure (PDF#80-1385). The peaks are very broad, indicating

that the powder is poorly crystallized. The bright-field TEM image (Figure 2(b)) shows a few-nm-sized Al₂O₃ powder. According to the SAED analysis (Figure 2(b)) the Al₂O₃ nano-crystals have a cubic symmetry; this result is in agreement with the XRD data.



(a)



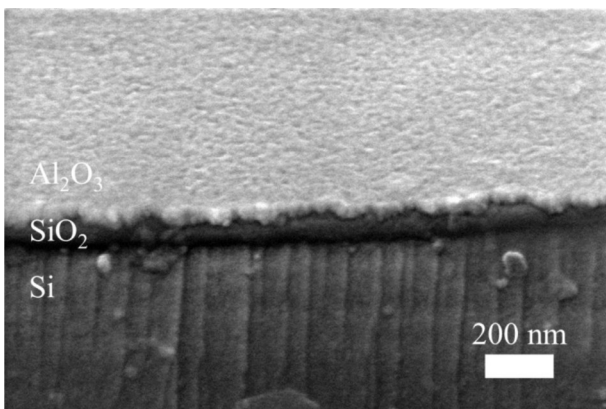
(b)

Figure 2: XRD pattern (a) and TEM image (bright field) (b) of Al₂O₃, after calcination at 900°C for 1 hour. The diffraction rings (inset of image b) were indexed with the cubic Al₂O₃ (PDF#80-1385)

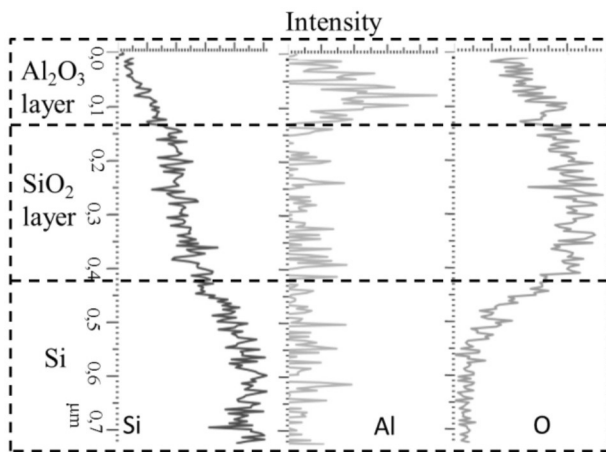
In accordance with these results, four layers of aluminum alkoxide solution were spin coated on the SiO₂/Si substrate and annealed for 1 hour at 900°C. The cross-section SEM micrograph of the prepared Al₂O₃/SiO₂/Si structure is shown in Figure 3(a). In order to determine the chemical composition a qualitative SEM-EDXS line analysis was performed across all the layers in the Al₂O₃/SiO₂/Si structure. (Figure 3(b)).

The surface of the upper layer is dense; the layer consists of a few-nm-sized grains. The SEM-EDXS analysis confirmed the presence of an upper Al₂O₃ layer on the SiO₂/Si substrate. However, the concentration profile of the Si shows that a small amount of Si was also detect-

ed within the Al_2O_3 layer, which can be related to the small spatial resolution of the EDXS analysis. Namely, when using a lower energy (below 10 keV) the information is coming from a depth of approximately 100–200 nm[15], i.e., greater than the thickness of the alumina layer, which is a few tens of nm. Therefore, besides the Al, a Si signal can also be detected. We should note that according to the SiO_2 - Al_2O_3 diagram, different aluminosilicates can be formed;[16] however, in the case of a thin, crystalline, alumina film on the silicon substrate, no silicon diffusion was reported in the literature. [4,5,6,10]



(a)



(b)

Figure 3: Cross-section SEM micrograph of the $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ structure, after annealing at 900°C for 1 hour (a). The EDS line analysis across the Al_2O_3 , SiO_2 and Si for Si, O and Al, performed at 5 keV (b). The cross-section and imaging were performed with the FIB microscope.

In order to analyze the Al_2O_3 film on the nanometer scale, the $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ structure was investigated by TEM. In Figure 4, a cross-section TEM micrograph of a ~ 20 -nm-thick Al_2O_3 film on a SiO_2/Si substrate is presented. The film consists of a few-nm-sized Al_2O_3 grains, as already observed by SEM analysis. According to the SAED analysis, the alumina grains have a cubic symme-

try. The results are in accordance with the XRD analysis performed on sol-gel-derived Al_2O_3 powder (Figure 2).

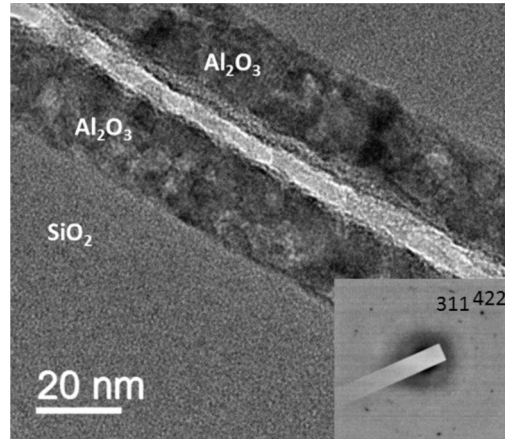


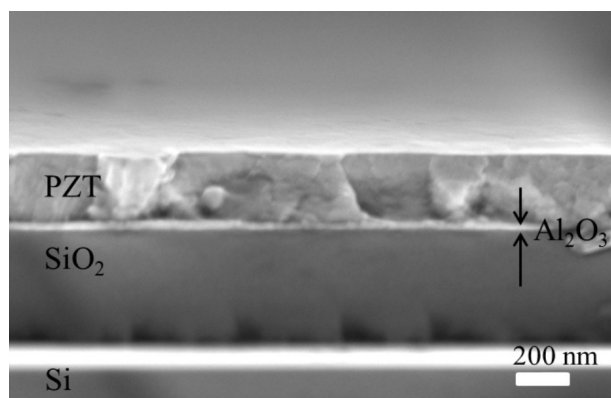
Figure 4: Cross-section TEM micrograph (bright field) of a polycrystalline Al_2O_3 thin film on a SiO_2/Si substrate, after firing at 900°C for 1 hour with the corresponding SAED patterns. The diffraction rings were indexed with the cubic Al_2O_3 (PDF#80-1385)

According to the SEM and TEM results, we can conclude that a continuous, dense, crystalline ~ 20 -nm-thick layer of aluminum oxide on the silicon substrate was formed after annealing at 900°C .

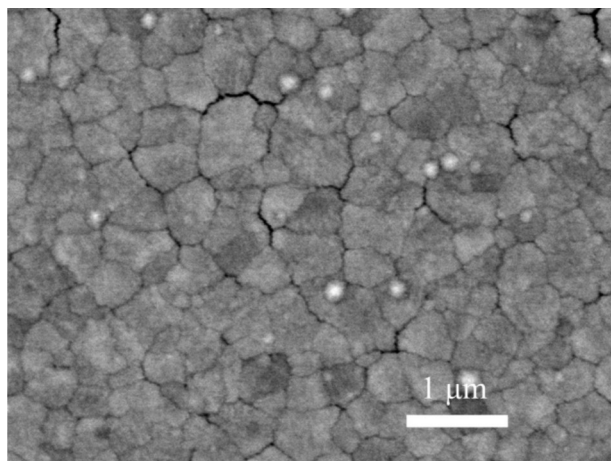
3.2 Characterization of the $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3/\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ structure

In the next step, the $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3$ solution was spin coated on the $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ substrate and the film was annealed two times, i.e., after the second and the fourth depositions of the solution, at 550°C for 15 min. A cross-section SEM micrograph of the $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3/\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ structure is shown in Figure 5(a); the surface of the upper PZT layer is shown in Figure 5(b). The PZT film on the $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ substrate is ~ 300 -nm-thick and the thickness is uniform within the investigated range. It consists of a few-hundred-nm-sized, irregularly shaped grains. In the surface microstructure, the boundaries between the grains are clearly visible. Besides larger PZT grains, some small, white, round inclusions of a lead-rich secondary phase are also seen at the PZT grain boundaries. A similar microstructure for a PZT thin film on a platinumized silicon substrate was observed by Kosec et al.[17] The authors explained that up to $4\text{-}\mu\text{m}$ -sized grains of PZT are formed due to the small number of nucleation sites.[17] The PbO secondary phase at the PZT surface was also observed by Bursill et al.[18]

In Figure 6, the X-ray powder-diffraction pattern of the $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3/\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ structure is shown. High-in-



(a)



(b)

Figure 5: SEM-BE micrographs of the $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3/\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ structure (a), the surface of the PZT layer on the $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ substrate (b), after annealing at 550°C .

tensity peaks marked with hkl indices can be ascribed to the randomly oriented perovskite PZT phase with the tetragonal symmetry; however, no {00l} reflections were detected. Evidently, the PZT film is a-axis oriented, which in other words means that the c-axis of the PZT unit cell is parallel with the $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ substrate. Such an orientation of the $\text{Pb}(\text{Zr,Ti})\text{O}_3$ film on the silicon substrate is a consequence of the tensile stresses within the multilayered structure that develop during cooling.[19,20] A low-intensity reflection at $2\theta=29^\circ$, which could be ascribed to PbO, was also observed. The XRD results are in accordance with the SEM analysis, where besides the larger perovskite PZT grains, smaller round inclusions of lead oxide at the grain boundaries between the PZT grains were observed (see Figure 5).

In order to analyze the $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3/\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ structure at the nano level the TEM analysis was performed (Figure 7(a)). An enlarged view of the PZT layer is shown in Figure 7(b) and the boundaries between the PZT- Al_2O_3 - SiO_2 layers in Figure 7(c). A dense, $\sim 300\text{-nm}$ -

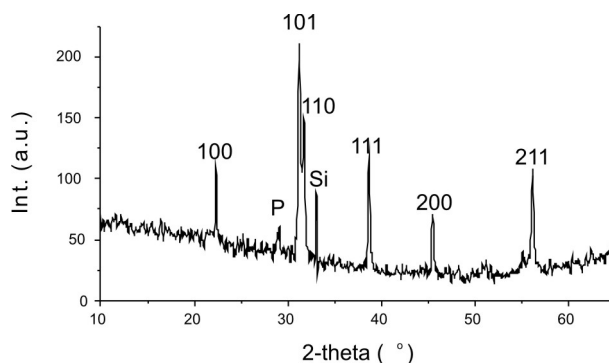


Figure 6: XRD pattern of the $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3/\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ structure after annealing at 550°C . Peaks belonging to the tetragonal $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3$ perovskite phase (ICSD 90473) are marked with hkl, the peak belonging to the silicon substrate (PDF 01-072-1088) is marked with Si, the peak marked with P could be indexed with the orthorhombic PbO (PDF 01-072-0094).

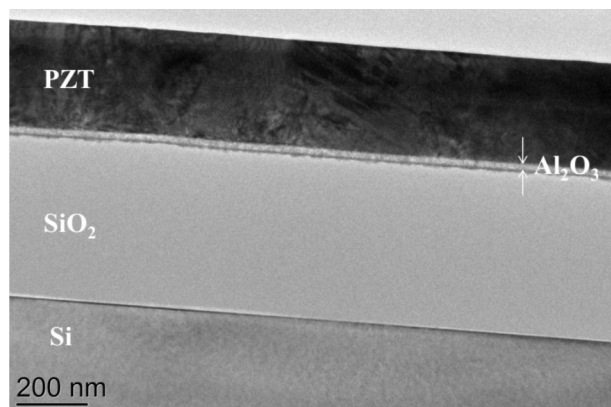
thick PZT layer is observed on the top of the thin polycrystalline alumina layer with a uniform thickness. The PZT layer consists of $\sim 300\text{-nm}$ -sized grains. Small pores are visible within the PZT layer. The SAED pattern of the PZT grain, shown in Figure 7(b), was indexed with the tetragonal $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3$ unit cell ($a, b=3.978 \text{ \AA}$ and $c=4.148 \text{ \AA}$, SG: P4mm, ICSD #90473). According to the diffraction pattern the PZT grain is oriented in the $\langle 001 \rangle$ zone axis. The c-axis of the perovskite grain is perpendicular to the observed plane, i.e., it is parallel to the $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ substrate. The result is in accordance with the XRD data, where an a-axis-oriented PZT film was observed (Figure 6).

However, a closer look at the structure (Figure 7(c)) shows that an intermediate layer of amorphous secondary phase is formed between the alumina and the SiO_2 . A maximum thickness of the secondary phase is around 10 nm.

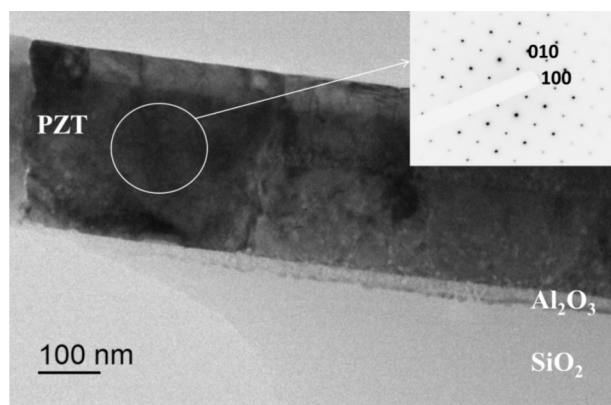
In order to determine the chemical composition of the secondary phase, a TEM-EDXS analysis was performed through all the layers, as shown in Figure 8.

According to the EDXS analysis, the intermediate layer below the Al_2O_3 contains Al, Si, O and Pb, indicating that PbO diffused through the alumina layer towards the substrate. In the PZT and alumina concentration profiles, silicon is also present, most probably due to the sputtering of silicon during the preparation of the TEM sample.

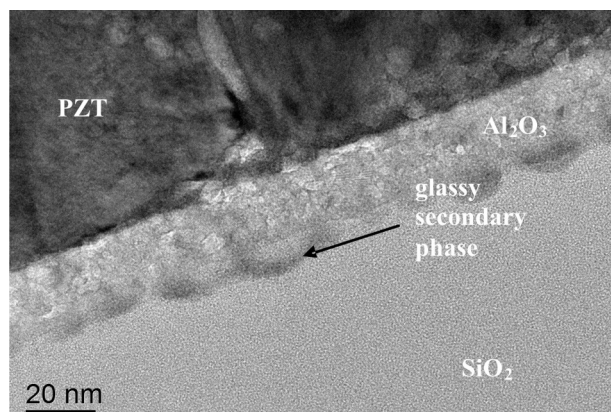
To conclude, although the nanosized Al-Si-Pb-O-containing amorphous phase was formed below the alumina layer, no lead-deficient pyrochlore phase was observed in the PZT film. Presumably, the small amount of diffusion of PbO from the PZT to the Si was compen-



(a)



(b)



(c)

Figure 7: Cross-section TEM micrographs (bright-field) of $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3/\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ structure (a), enlarged view of the PZT layer with SAED of the tetragonal perovskite PZT grain in the $\langle 100 \rangle$ zone axis (b) and the boundaries between the SiO_2 , Al_2O_3 , and PZT layers (c).

sated with an excess of PbO used in the starting precursors. It seems that the alumina layer is not thick enough (~ 20 nm) to prevent lead oxide diffusion from the PZT towards the Si substrate completely, and thus, a thicker alumina layer would be needed.

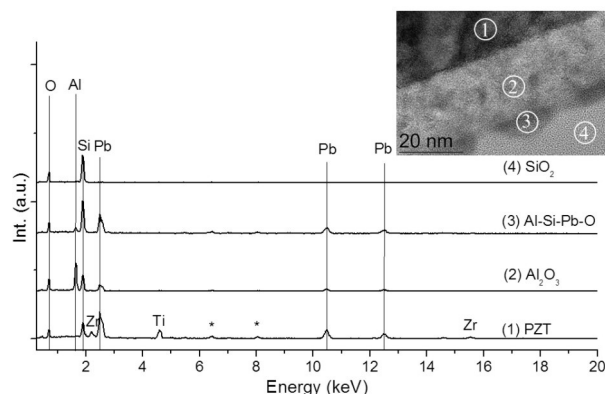


Figure 8: TEM - EDXS patterns obtained from the $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3/\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ structure. Inset: On the HR-TEM image the regions where the analyses were performed are marked.

4 Conclusions

A dense, nanocrystalline layer of γ -alumina oxide was successfully synthesized on a silicon substrate using the sol-gel method. After the deposition and annealing at 900°C for 1 hour an ~ 20 -nm-thick alumina layer was obtained, and investigated as a buffer layer between the $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3$ (PZT) layer and the silicon substrate. An a-axis-oriented tetragonal PZT film was obtained on the $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Si}$ substrate after annealing at 550°C . The PZT layer is ~ 300 -nm-thick and consists of ~ 300 -nm-sized grains. According to the TEM-EDXS analysis, an additional, up to 10 nm, Al-Si-Pb-O phase was observed below the alumina layer, indicating that a minor diffusion of lead oxide through the alumina layer into the silicon took place during the annealing at 550°C .

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