Compositional and Microstructural Study of Sol-Gel-Derived PbZr$_{0.3}$Ti$_{0.7}$O$_3$/Al$_2$O$_3$/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$_2$O$_3$/SiO$_2$/Si thin-film structures. The PbZr$_{0.3}$Ti$_{0.7}$O$_3$ (PZT) and Al$_2$O$_3$ 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$_2$O$_3$ and SiO$_2$ layers.

This work is dedicated to the late Professor Marija Kosec

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

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)$_{0.5}$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$_2$O$_3$[4,5,6], Ba(Mg$_{1/3}$Ta$_{2/3}$)$_2$O$_3$[7], MgAl$_2$O$_4$[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$_{0.53}$Ti$_{0.47}$)$_{0.5}$O$_3$ and Si substrate, were prepared by a sol–gel route[4], by chemical vapor deposition (CVD)[5,6] or by a com-
Combination 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 Pb(Zr,Ti)O₃ 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 PbZr₀.₃Ti₀.₇O₃/Al₂O₃/SiO₂/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 PbZr₀.₃Ti₀.₇O₃ 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, (Al(O-secC₄H₉)₃, Aldrich) in 2-methoxyethanol (CH₃-O-CH₂-CH₂-OH (2-MOE), Alfa Aesar). The solution was then intensively stirred in a dry box for 1 hour.

A precursor solution with the composition PbZr₀.₃Ti₀.₇O₃ and 10% excess of PbO was prepared in an atmosphere of dry nitrogen by mixing dehydrated lead acetate (Pb(OAc)₂, Alfa Aesar) titanium iso-propoxide (Ti(O-iC₃H₇)₄, Alfa Aesar) and zirconium iso-propoxide (Zr(O-iC₃H₇)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 (HCONH₂, Alfa Aesar) was added to the solution. A detailed description of the Pb(Zr,Ti)O₃ 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 SiO₂/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 Al₂O₃/SiO₂/Si structure was annealed at 900°C for one hour with a heating rate of ~14°C/min. Later, four layers of PbZr₀.₃Ti₀.₇O₃ solution were deposited on an Al₂O₃/SiO₂/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 PbZr₀.₃Ti₀.₇O₃ layer (subsequently denoted as the PZT layer) the PZT/Al₂O₃/SiO₂/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 (CuKα radiation, Philips PW 1710) in the range 2θ=10°–65° 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.

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.

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)).

![Figure 1: TG/DTA curves of aluminum alkoxide solution performed from 20°C to 1400°C.](image1)

![Figure 2: XRD pattern (a) and TEM image (bright field) (b) of Al₂O₃ after calcination at 900°C for 1 hour.](image2)
ed within the Al₂O₃ 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 SiO₂-Al₂O₃ 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]

Figure 3: Cross-section SEM micrograph of the Al₂O₃/SiO₂/Si structure, after annealing at 900°C for 1 hour (a). The EDS line analysis across the Al₂O₃, SiO₂, 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 Al₂O₃ film on the nanometer scale, the Al₂O₃/SiO₂/Si structure was investigated by TEM. In Figure 4, a cross-section TEM micrograph of a ~20-nm-thick Al₂O₃ film on a SiO₂/Si substrate is presented. The film consists of a few-nm-sized Al₂O₃ grains, as already observed by SEM analysis. According to the SAED analysis, the alumina grains have a cubic symmetry. The results are in accordance with the XRD analysis performed on sol-gel-derived Al₂O₃ powder (Figure 2).

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 PbZr₀.₃Ti₀.₇O₃/Al₂O₃/SiO₂/Si structure

In the next step, the PbZr₀.₃Ti₀.₇O₃ solution was spin coated on the Al₂O₃/SiO₂/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 PbZr₀.₃Ti₀.₇O₃/Al₂O₃/SiO₂/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 Al₂O₃/SiO₂/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 platinized silicon substrate was observed by Kosec et al.[17] The authors explained that up to 4-μm-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 Burssill et al.[18]

In Figure 6, the X-ray powder-diffraction pattern of the PbZr₀.₃Ti₀.₇O₃/Al₂O₃/SiO₂/Si structure is shown. High-in-
Intensity peaks marked with hkl indices can be ascribed to the randomly oriented perovskite PZT phase with 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 Al2O3/SiO2/Si substrate. Such an orientation of the Pb(Zr, Ti)O3 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 2Θ=29°, 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 PbZr0.3Ti0.7O3/Al2O3/SiO2/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–Al2O3–SiO2 layers in Figure 7(c). A dense, ~300-nm-thick PZT layer is observed on the top of the thin polycrystalline alumina layer with a uniform thickness. The PZT layer consists of ~300-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 PbZr0.3Ti0.7O3 unit cell (a, b=3.978 Å and c=4.148 Å, SG: P4mm, ICSD #90473). According to the diffraction pattern the PZT grain is oriented in the <001> zone axis. The c-axis of the perovskite grain is perpendicular to the observed plane, i.e., it is parallel to the Al2O3/SiO2/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 SiO2. 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 Al2O3 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-
sated with an excess of PbO used in the starting precur-
sors. 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 7: Cross-section TEM micrographs (bright-field) of PbZr0.3Ti0.7O3/Al2O3/SiO2/Si structure (a), enlarged view of the PZT layer with SAED of the tetragonal perovskite PZT grain in the <100> zone axis (b) and the boundaries between the SiO2, Al2O3, and PZT layers (c).

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 PbZr0.3Ti0.7O3 (PZT) layer and the silicon substrate. An a-axis-oriented tetragonal PZT film was obtained on the Al2O3/SiO2/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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6 References

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