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Atomic layer deposition of PbZrO_3 thin films

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Abstract

In this paper, we report on the preparation of lead zirconate films for the first time using atomic layer deposition in an attempt to investigate some of the film properties and also to evaluate possible use of the precursor combination to prepare more complex lead titanate zirconate. In the depositions tetraphenyl lead (Ph_4Pb) was used as the lead and zirconium 2,2,6,6-tetramethyl-3,5-heptadionate ($\text{Zr}(\text{thd})_4$) as the zirconium precursor, while ozone was used as the oxygen source. Film growth, stoichiometry and quality were studied using different pulsing ratios at deposition temperatures of 275 and 300 °C. According to X-ray diffraction, the crystalline perovskite phase was observed when films deposited on $\text{SrTiO}_3(1\ 0\ 0)$ were annealed at 600 °C. Surface roughness was reduced for lead deficient films as well as in annealed samples.

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1. Introduction

Lead zirconate (PbZrO_3) is an antiferroelectric material at room temperature [1]. The ferroelectric state can be induced when lead zirconate is subjected to a sufficiently large electric field. This change in bulk material occurs near the Curie point, which is 233 °C for PbZrO_3 [1], but in thin films a typical double hysteresis loop is observed already at room temperature [2]. Transition from antiferroelectric to ferroelectric phase leads to a large volume expansion due to the difference in the size of the unit cells [3,4]. When the applied field is removed a large amount of charge is also released [2]. This feature is utilized in many applications such as transducers [5,6], charge storage devices [2,5,7–9], microelectromechanical systems (MEMS) [2,6,8,9] and microsensors [2,3]. The main interest in PbZrO_3 (PZ) thin films is probably due to the solid solution which PZ forms together with lead titanate (PbTiO_3) producing lead zirconate titanate (PZT). Polarization states of perovskite PZT are utilized in FeRAM, which enables nonvolatile memory applications [10].

Other applications, such as sensors, actuators and transducers, exploit the pyroelectricity and piezoelectricity of PZT [11,12].

Lead zirconate films have been deposited by several deposition techniques where selected examples include: laser ablation [2], reactive magnetron sputtering [13], wet chemical deposition studies such as sol-gel [8], dip-coating [14] and chemical solution deposition [15]. However, only a few chemical vapour deposition (CVD) studies have been reported [16–19] and they are discussed here in a more detailed way due to the similarity of CVD with atomic layer deposition (ALD). Lee and Woo [16] used a plasma-enhanced CVD method to deposit PbZrO_3 thin films on $\text{Si}(1\ 0\ 0)$ substrates. They used tetraethyl lead ($\text{Pb}(\text{C}_2\text{H}_5)_4$) together with zirconium tetra-tert-butoxide ($\text{Zr}(\text{O}(\text{CH}_3)_3)_4$) as the metal precursors and oxygen as the oxidizing source. A deposition temperature of 250 °C was used but annealing was found to be necessary to obtain crystalline films. However, after annealing at 850 °C still some metallic lead and zirconium oxide was observed by X-ray diffraction (XRD) together with perovskite PZ phase. Another observation was that excess lead promoted the crystallization. Same precursor combination was used by Moret et al. [17]. They deposited PZ films on SrTiO_3 (STO) substrates by the MOCVD method. At the deposition temperature of 700 °C, cubic PZ was observed to grow epitaxially on cubic STO. However, during the cooling down, cubic PZ was transformed

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to an antiferroelectric, orthorhombic structure and the epitaxiality was lost. On the other hand, Bai et al. [19] succeeded to grow epitaxial PZ thin films on single crystalline STO substrates by MOCVD. They used lead β -diketonate $\text{Pb}(\text{thd})_2$ (thd = bis(2,2,6,6-tetramethyl-3,5-heptadionato)) together with $\text{Zr}(\text{thd})_4$ as precursors and oxygen as the oxidizing source. Deposition temperatures between 650 and 750 °C were employed.

Atomic layer deposition (ALD or ALCVD) is an advanced version of the CVD method. It is based on self-limiting film growth mechanism which is achieved by alternately pulsing the precursors. Between the precursor pulses the reactor space is purged with inert gas to remove excess precursor and possible by-products. For general reviews of ALD, see the recent ones [20–23]. Recently, we have studied the ALD deposition of PbO_2 [24] and PbTiO_3 [25]. Also binary ALD processes for ZrO_2 have been previously reported using different volatile precursors [26–30]. In this paper we report the ALD deposition of PbZrO_3 thin films at 275 and 300 °C using Ph_4Pb and $\text{Zr}(\text{thd})_4$ precursors together with ozone.

2. Experimental

Tetraphenyl lead (Ph_4Pb) (Acros Organics, 97%), zirconium 2,2,6,6-tetramethyl-3,5-heptadionato ($\text{Zr}(\text{thd})_4$) (Strem Chemicals, 99% or synthesized according to Ref. [31]) were used as metal precursors. Properties of these precursors and their suitability for ALD have been previously studied [24,26]. The oxygen source for the lead and zirconium precursors was ozone. Ozone was generated from oxygen (>99.999%) in an ozone generator (Fischer model 502).

The deposition of PbZrO_3 thin films was performed in a flow-type F-120 ALD reactor manufactured by ASM Microchemistry Ltd. The reactor was operated under a pressure of about 3 mbar. Nitrogen (>99.999%) gas, generated in a Nitrox UHPN 3000-1 nitrogen generator, was used as a carrier and purging gas. The precursors were evaporated inside the reactor at temperatures of 160 and 130 °C for Ph_4Pb and $\text{Zr}(\text{thd})_4$, respectively. Depositions of PbZrO_3 thin films were performed at temperatures of 275 and 300 °C onto Si(100). After optimizing the process, MgO buffered Si(1 0 0) [32] and SrTiO_3 (1 0 0) substrates were also used in some selected depositions.

Reflectance spectra were measured in a Hitachi U-2000 double beam spectrophotometer. Thicknesses of the deposited films were calculated by the optical fitting method described by Ylilammi and Ranta-aho [33]. The Pb to Zr ratio was measured using Philips PW 1480 X-ray fluorescence (XRF) spectrometer equipped with a Rh X-ray tube. Data analysis was performed with the Uniquant 4.34 program, which utilizes the de Jongh Kappa model to calculate simultaneously the composition and mass thickness of an unknown sample [34]. The XRF results were calibrated by using some samples measured by RBS (Rutherford Backscattering Spectrometry). RBS was also used to study atom depth distributions in the as-deposited and annealed samples. The RBS experiments were performed at the Accelerator Laboratory of the University of Helsinki. A beam of 2.75 MeV ^7Li ions from a 5 MV EGP-10-II tandem

accelerator was used. The RBS data analyses were accomplished by the codes SIMNRA and GISA [35,36].

Selected samples were annealed in a rapid thermal annealing (RTA) oven (PEO 601, ATV Technologie GmbH, Germany) in N_2 or O_2 (>99.999%) atmosphere at 500–700 °C for 10 min at atmospheric pressure. Heating rates between 20 and 90 °C per minute were tested. Crystallite orientations and crystallinity of the deposited films were determined by XRD using $\text{Cu K}\alpha$ radiation in a Philips MPD 1880 diffractometer. Rocking curve measurements were performed with a Bruker axS D8 Advance diffractometer. Surface morphology was studied by a Nanoscope III atomic force microscope (Digital Instruments) operated in tapping mode. Samples were measured with a scanning frequency of 0.5–1 Hz. Several wide scan (5–10 μm) were performed from different parts of samples to check the uniformity of the sample. Final images were measured from a scanning area of 2 $\mu\text{m} \times 2 \mu\text{m}$. Roughness values were calculated as root mean square values (rms).

3. Results

Binary oxides and their optimum growth temperatures determine the temperature range where ternary or more complex oxides can be deposited. Growth of lead oxide from Ph_4Pb exhibits a constant growth rate of 0.13 Å/cycle only in a quite narrow temperature range of 200–250 °C. At 300 °C the growth is still self-limiting but the growth rate is lower being only 0.10 Å/cycle. Therefore maximum deposition temperature for PbTiO_3 is restricted to 300 °C [25]. With regard to depositions of ZrO_2 by ALD, several precursors have been studied [26–29] but $\text{Zr}(\text{thd})_4$ was selected in the present study due to its reasonably low growth rate matching the low growth rate of Ph_4Pb . Matching of the deposition rates is assumed to produce the desired films with a pulsing ratio close to 1:1 increasing the reproducibility of film stoichiometry. Although the optimal surface controlled deposition region for $\text{Zr}(\text{thd})_2$ was previously reported to be at 375–400 °C [26], PbZrO_3 films were successfully deposited at somewhat lower temperatures.

Ternary PbZrO_3 thin films were deposited by alternating the $\text{Ph}_4\text{Pb}/\text{O}_3$ and $\text{Zr}(\text{thd})_4/\text{O}_3$ cycles in order to control the film composition, see Fig. 1. The optimum pulsing ratio of the Pb:Zr precursor pulsing cycles was 3–3.5 in the deposition temperature of 250 °C. This resulted in a Pb/Zr atomic ratio of about 1. From Fig. 1 it can be also seen that at a higher deposition temperature of 300 °C, a higher Pb:Zr precursor pulsing ratio is needed to get nearly stoichiometric film. However, stoichiometric PbZrO_3 films can be grown at deposition temperatures 275 and 300 °C by carefully selecting the pulsing ratio.

Even though binary zirconium and lead oxides have comparable growth rates at the temperatures studied, Pb:Zr pulsing ratios of 7:2 and 6:1 were needed to obtain closely stoichiometric films at 275 and 300 °C, respectively. This is most probably due to the fact that different surfaces, as compared to the binary films, induce changes in the precursor reactivity and adsorption behavior on the surface. Surface chemistry also has a distinct influence on thin film growth rates,

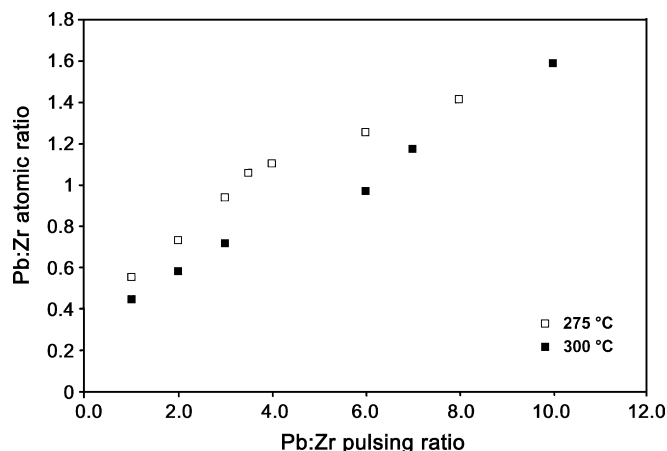


Fig. 1. The Pb/Zr atomic ratio in PbZrO₃ films as a function of the pulsing ratio between the Ph₄Pb/O₃ and Zr(thd)₄/O₃ cycles. Films were deposited on Si(1 0 0) substrates at 275 and 300 °C.

which can be determined by comparing the observed film thickness with the theoretical thickness calculated from the growth rates of the binary oxides. Interestingly, compared to binary processes the relative growth rate was increased by 150% in the case of the deposition of stoichiometric PbZrO₃ (Fig. 2). However, the growth rate still remains quite low, being 0.15 Å/cycle.

This kind of increase in the relative growth rates compared to the theoretical growth from separate oxides has also been observed in our previous study of PbTiO₃ thin films [25]. In contrast, a decrease in relative growth rates of ternary oxides has been observed in the case of ALD-processed SrTiO₃ [37], LaGaO₃ [38] and LaAlO₃ [39].

In the case of PbZrO₃, the relative growth rate was nearly 100% compared to the theoretical thickness calculated from the growth rates of the binary oxides when the atomic ratio of Pb/Zr in the thin films was 0.6 (Fig. 2). When the relative amount of Pb pulses was increased, the relative growth rate was also increased. After the Pb/Zr atomic ratio reaches the near stoichiometric value of 0.9, the maximum relative growth rate is obtained which then stays constant until after the value of 1.25 the growth rate decreases again near the value of 100%. It

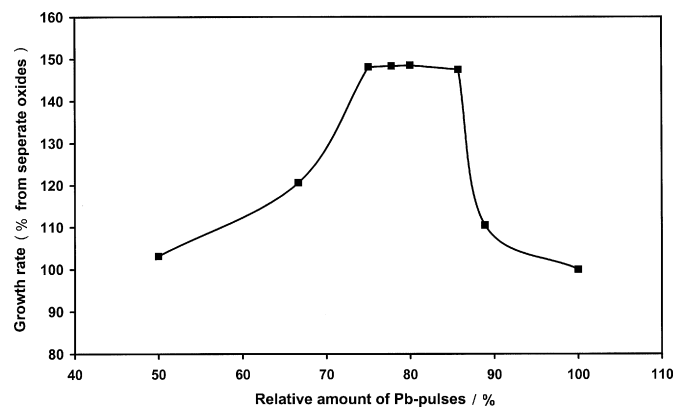


Fig. 2. The PbZrO₃ growth rate compared to the binary lead oxide and zirconium oxide processes. Films were deposited at 275 °C.

seems that this mixed surface near stoichiometric PZ somehow promotes the precursor adsorption and thus increases the growth rate. However, further studies would be needed to fully understand this phenomenon.

The growth rate shows an almost linear dependence on the number of cycles as seen in Fig. 3. The growth rate (total number of cycles divided by the film thickness) saturates at 0.12 Å per cycle when PbZrO₃ is deposited at 275 °C. This confirms that the thickness of the thin film can be controlled by simply monitoring the number of ALD deposition cycles.

XRD patterns revealed that the as-deposited thin films were crystalline. Various lead and zirconium oxide phases were detected depending on the lead to zirconium ratio of the films. Zirconium-rich films crystallized forming the tetragonal ZrO₂ phase [40]. In nearly stoichiometric films, as well as in lead-rich films, both cubic ZrO₂ and orthorhombic PbO₂ phases were detected [41]. However, crystalline PbZrO₃ perovskite phase was not observed in the as-deposited films on Si(1 0 0), MgO-buffered Si(1 0 0) or SrTiO₃(1 0 0). In previous MOCVD studies, crystalline lead zirconate was obtained when single-crystalline SrTiO₃ or LaAlO₃ was used as a substrate [17,19]. In contrast, when deposited onto Si substrates by PECVD the perovskite phase was not observed until after an RTA treatment at 850 °C [16]. Even then, additional peaks originating from metallic lead and zirconium oxide were present. In the present study, crystallinity was clearly induced by annealing but the presence of the perovskite phase could not be confirmed on the basis of the XRD data when deposited on Si(1 0 0). Instead, peaks originating from lead and zirconium oxide were identified. Independent of lead to zirconium ratio in the films, both tetragonal ZrO₂ and PbO₂ were detected. Only the intensities of those reflections were changed when the content of the films were changed. The annealing temperature was raised up to 700 °C, but this was clearly the maximum due to poor adherence of the films. Changing heating rates did not bring any improvements in the crystallinity either. Also experiments using Si(1 0 0) buffered by ALD-grown MgO did not produce crystalline PbZrO₃, most probably because the as-deposited MgO is only weakly (1 1 1) oriented and partly amorphous, judging from its relatively high FWHM value [32].

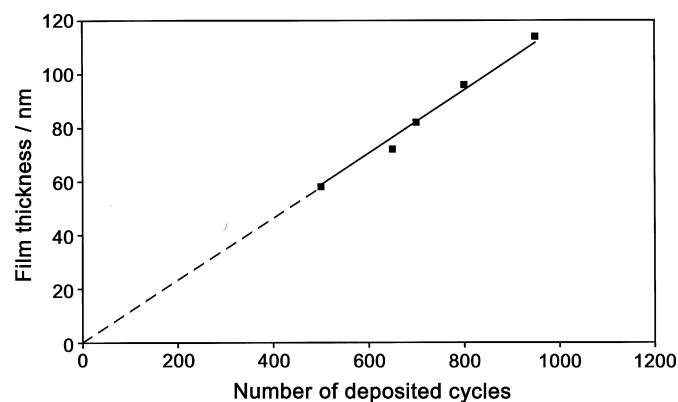


Fig. 3. The dependence of PbZrO₃ film thickness on the number of deposition cycles. The Pb:Zr pulsing ratio of 7:2 and the deposition temperature of 275 °C were employed.

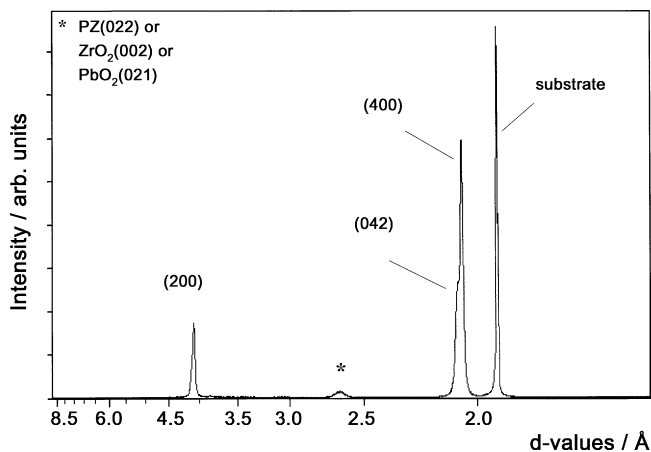


Fig. 4. XRD pattern of PbZrO₃ film deposited on SrTiO₃ at 275 °C and annealed in oxygen at 600 °C.

Theoretically, deposition of PZ thin films on single crystalline MgO substrate should be successful because of the low lattice mismatch of 1.2% compared to that of Si, which has a mismatch of 8.3%.

Finally crystalline PbZrO₃ was obtained when films were deposited on single crystalline SrTiO₃ but even in this case, a post-deposition annealing was necessary. Oriented perovskite films were thus obtained after annealing for 10 min at 600 °C in oxygen atmosphere. Fig. 4 shows the diffraction patterns for the nearly stoichiometric films deposited at 275 °C with a Pb/Zr atomic ratio of 1.1. The most intense reflection is (4 0 0) and the full-width half-maximum (FWHM) values for the three strongest peaks are between 0.25° and 0.34°. Three different phases have a reflection near the *d*-value of 2.65 Å, see Fig. 4, namely orthorhombic PbZrO₃, orthorhombic PbO₂ and tetragonal ZrO₂. Because of this, identification of this reflection cannot be unambiguous. Nevertheless, the 0 2 2 reflection of the PbZrO₃ appears to be the most probable. The Maximum on

the rocking curve was obtained for both the (2 0 0) and the (4 0 0) PbZrO₃ reflections. However, peaks were broad and thereby show that the film has a strong texture but is not epitaxial.

The elemental distributions in depth were studied by RBS for both the as-deposited and the annealed films. Fig. 5 shows spectra of two samples and the Pb and Zr depth distributions before and after annealing for a 50 nm sample having an initial Pb/Zr atomic ratio of about 1.1. The Zr distribution stays quite constant throughout the film, while the Pb concentration slightly increases with depth. Before annealing, the Zr concentration falls off at a lower thickness in the interfacial region. A small (about 1 at.%) Sn impurity was also observed in the film, which originates most likely from the commercial lead precursor.

Annealing at 600 °C affects the Pb distribution only little, but tends to move some of the Zr from the film towards the interface and into the silicon substrate. The Zr/Pb ratio shows the same slightly decreasing behavior towards the interface for both the as-deposited and the annealed samples. This verifies that excluding the interfacial region, the film stays relatively stable regardless of annealing at a temperature as high as 600 °C.

The surface morphologies of selected samples deposited on silicon and on STO were analyzed by AFM. The rms values of as-deposited zirconium-deficient films deposited on silicon at 275 °C were rather high being around 23 nm for 100 nm thick films. Interestingly, the rms value was found to be greatly reduced when a slightly lead-deficient film was analyzed and it was only around 7 nm, for a 90 nm thick film with the Pb/Zr ratio of 0.9. Annealing at 600 °C in oxygen atmosphere also reduced the rms values at both deposition temperatures, viz. 275 and 300 °C. The rms value was somewhat decreased from 23 nm measured for as-deposited films to 18 nm at 275 °C. At 300 °C the rms values were 19 and 17 nm for as-deposited and annealed films, respectively. Pb/Zr atomic ratio in these films was around 1.1. Previously, similar rms values were observed

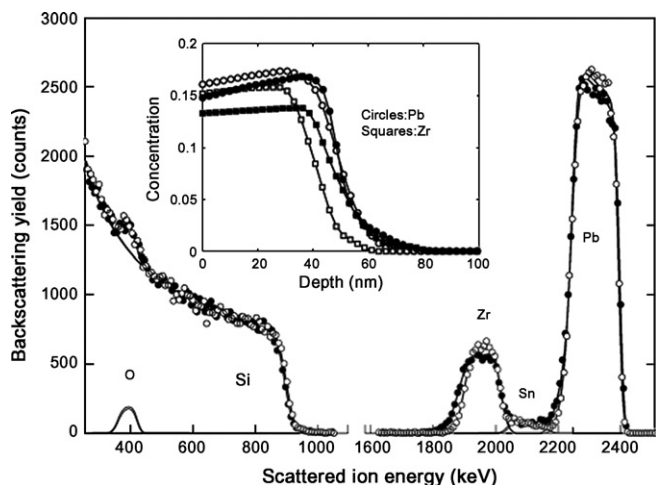


Fig. 5. Rutherford backscattering spectra for 2.75 MeV ⁷Li ions incident on the 50 nm lead zirconate sample. The open symbols stand for the as-deposited sample while the solid symbols refer to the sample annealed in 600 °C. The lines connecting the experimental symbols in the spectra are the theoretical simulations. The inset shows the concentration depth distributions of Pb and Zr as derived from the spectra.

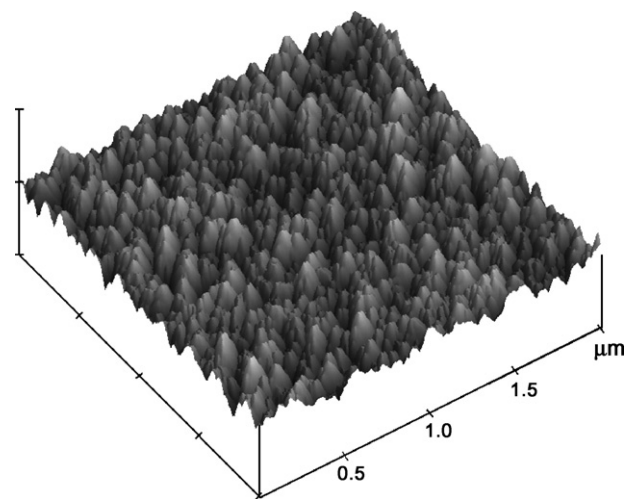


Fig. 6. AFM image of PbZrO₃ film deposited onto STO substrate at 275 °C. The image shows a 70 nm thick film with an image size of 2 μm × 2 μm. The depth scale is 70 nm from black to white.

for a 210 nm thick as-deposited PbTiO_3 film, deposited at 250 °C, where the rms value was 23.8 nm [25]. In the case of PbTiO_3 , the roughness was slightly increased up to a value of 27.4 nm after annealing the samples in oxygen atmosphere. One possible explanation for the high roughness values for Pb-based ternary processes could be the high mobility of lead on the substrate surface. Another reason in the case PbZrO_3 could be that when perovskite films crystallize, the film will orientate and reduce surface roughness. This conclusion was made since films on STO had much lower rms values than those on Si(1 0 0). Annealed PbZrO_3 on STO showed an rms value of 5.8 nm for lead rich films, see Fig. 6.

4. Conclusions

Growth of the ternary PbZrO_3 thin films was studied at 275 and 300 °C using ALD. Ph_4Pb together with $\text{Zr}(\text{thd})_4$ was found to be a promising precursor combination for the fabrication of the more complex PZT films. The atomic ratio of PbZrO_3 thin films could be changed when precursor combinations $\text{Ph}_4\text{Pb}/\text{O}_3$ and $\text{Zr}(\text{thd})_4/\text{O}_3$ were alternately pulsed. Stoichiometric PbZrO_3 films could be obtained at deposition temperatures of 275 and 300 °C when a suitable Pb/Zr pulsing ratio was selected. The film growth was reproducible and a linear dependence of the film thickness on the number of deposition cycles was observed which is typical for ALD growth mechanism. Films deposited on Si(1 0 0), MgO-buffered Si(1 0 0) and $\text{SrTiO}_3(1 0 0)$ were only partly crystalline and annealing was necessary to obtain the crystalline perovskite phase, but even after annealing the perovskite phase was observed only on STO. According to RBS, the atomic ratio stays relatively stable also after annealing. High mobility of lead was believed to be the reason for the high roughness values determined by AFM.

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