Effect of LaNiO₃ electrodes and lead oxide excess on chemical solution deposition derived Pb(ZrₓTi₁₋ₓ)O₃ films

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1. Introduction

Thin PbZrₜ₁₋ₓO₃ (PZT) films have excellent ferroelectric and piezoelectric properties which make them useful for sensors, actuators and memory applications [1–4]. Pt is often integrated as an electrode in PZT devices because of its stability at high temperature, low leakage current and high electrical conductivity [5]. However, in addition to its high cost, Pt has several disadvantages such as poor adhesion to the silicon substrate and a large thermal expansion coefficient mismatch with PZT. The poor adhesion is typically solved by deposition of a Ti intermediate adhesion layer. The main disadvantage of PZT/Pt device is the low ferroelectric fatigue limit that causes a severe decrease in the ferroelectric properties after 10⁷–10⁸ operating cycles [3,6,7]. The two main reasons for the fast fatigue in PZT/Pt system are thought to be: formation of oxygen vacancies in the PZT films during operation cycles [7,8] and the presence of Pyrochlore (Py) phase [3] that pinned the domain switching.

Lanthanum nickel oxide (LNO) is a conducting oxide which has attracted great attention in recent years due to its ability to drastically improve the ferroelectric fatigue [7,9] of PZT. LNO has lattice parameter of 0.384 nm and its typical film resistivity at room temperature is in the 300 μΩ·cm to 2000 μΩ·cm range [10]. Furthermore, LNO structure is compatible with PZT, since both have perovskite ABO₃ type unit cell [6] with 0.384 nm and 0.404 nm lattice constant for LNO and PZT respectively. Hence, LNO is an excellent candidate in coupling with PZT devices. The remnant polarization (Pr) and coercive field (Ec) of PZT/LNO have been reported to improve in comparison with PZT/Pt system.

It was suggested that the improved ferroelectric properties were due to better PZT interface with LNO electrodes in comparison with Pt [11] electrodes.

LNO electrodes can be made by different techniques such as pulsed laser ablation [12], r.f. magnetron sputtering [6], and chemical solution deposition (CSD) methods. Specifically, the microstructure of LNO and its influence on the PZT properties were studied as a function of PbO excess. Conditions to minimize the Pyrochlore phase and porosity were found. Remnant polarization, coercive field and fatigue limit were improved in the PZT/LNO films relative to the PZT/Pt films. Additionally, the PZT crystallization temperature over LNO was 500 °C, about ~50 °C lower than over Pt. The crystallization temperature reported here is amongst the lowest values for CSD-based PZT films.

2. Experimental details

LNO electrodes were prepared using the CSD method. Solution precursors were prepared by dissolving lanthanum acetate hydrate C₃H₅LaO₅·xH₂O (99.9%, Sigma-Aldrich, Steinheim, Germany) in a mixture of distilled water and glacial acetic acid C₄H₇O₂ (99.8%, Gadot, Netanya, Israel) in a molar ratio of 1:15:144 for lanthanum acetate hydrate, distilled water and glacial acetic acid respectively at 75 °C for 1 h. An equi-molar amount of nickel acetate tetrahydrate (98% Sigma-Aldrich) was dissolved in glacial acetic acid in a molar ratio of 1:25 for
nickel acetate tetrahydrate and acetic acid respectively at 75 °C for 1 h. These solutions were stirred together at 75 °C for 1 h. The green final precursor’s concentration was 0.2 M and it’s assay was 4.5% wt. The precursor had a shelf life of more than one year without any visual phase separation and without any changes in the final electrode properties. LNO electrodes were prepared by spin coating at 3000 rpm for 60 s, acceleration of 1000 rpm/s, followed by pyrolysis on a hot plate at 350 °C for 2 min and a final annealing step at 700 °C for 20 min in Air. Due to the relatively low concentration of the LNO precursor, the resulting film thickness per cycle was ~25 nm. The deposition cycle was repeated till the desired LNO thickness in the range of 25–225 nm was achieved.

The detailed preparation of the PZT precursors and films is described elsewhere [2–4]. In the present work PZT precursors of with 10% and 30% PbO excess were prepared and diluted with 1-octanol in order to deposit defect-free PZT films [4]. The CSD route for PZT deposition over LNO and Pt electrodes was as follows: 3 cycles of spinning at 3000 rpm for 1 min with acceleration of 1000 rpm/s, pyrolysis on a hot-plate at 300 °C for 1 min, and a final annealing step at 650–500 °C in air for 10–60 min. Upper Au circular electrodes (500 μm diameter), were deposited by evaporation (Edwards E306A, Crawley, UK), using a contact mask technique. The film surface and cross-sectional microstructure were studied with a high-resolution field emission gun equipped with a scanning electron microscope (LEO 982, Cambridge, U.K). Conditions included a 4 kV accelerating voltage and a 4 to 5 mm working distance, using an in-lens detector of secondary electrons. The grain size was determined by the equivalent area method without a correction factor using an image analysis software (Image tool, Copyright UTHSCSA) based on the HRSEM pictures. In order to enhance the grain boundary definition, the nanoparticles were analyzed when image is viewed in the threshold mode. Only particles with well-defined boundaries were considered as individual grains.

The crystalline phases were detected by X-ray diffraction (XRD), using a Siemens D5000 powder diffractometer instrument (Siemens, Karlsruhe, Germany). Atomic force microscopy (AFM) analyses were performed at scanning area of 2.5×2.5 μm² in a non-contact mode using an Agilent 5500 system (Tempe, USA). For the LNO electrode resistivity measurements a four point probe method was used with Veeco FPP5000 system (Tucson, USA) and a distance of 1.59 mm between the probe tips. An elemental distribution depth profile in the LNO film was obtained with secondary ion mass spectrometer, SIMS (Cameca ims-4 f, Paris, France). The sample was sputtered using a 3 keV Cs+ primary ions source by monitoring O, Si, Ni, La, Ti, Zr and Pb secondary ions from a 40 μm² area. The fatigue and hysteresis measurements were tested using a Sawyer–Tower bridge. The applied voltage was a 15 V (peak to peak) sine wave with a 1 kHz or 10 kHz frequency for hysteresis and fatigue measurements, respectively.

3. Results and discussion

3.1. Film morphology and resistivity

The surface morphology of LNO electrodes with different thickness are shown in Fig. 1a-c. It can be seen that the size of the LNO grains increases with the thickness. As shown in Fig. 1d, the average LNO grain size is 38 nm and 58 nm for electrode thickness of 75 nm and 225 nm, respectively. For defect-free bulk materials, the grain size (D), is typically proportional to the square root of annealing time [17] (i.e. D ∝ t⁰.⁵). Our experimental results indicate that for LNO electrode the grain size is proportional to 0.4 power of the thickness (Fig. 1d). The shift in the power value in comparison with the literature [17] can be explained by two factors: the experimental value is based on an LNO film rather than bulk, and the film is probably not defect free. Defects can pin the grain growth and lead to a smaller than expected grain

Fig. 1. HRSEM film morphology of LNO at thickness of (a) 75 nm, (b) 125 nm, (c) 225 nm and (d) grain size vs. thickness; bar-200 nm.
size. In addition, in the multistage film deposition process, each layer in the film is being heated to successively shorter time — therefore smaller grains could be expected relative to the bulk case. Both effects are expected to give rise to lower power dependence relative to the bulk case.

The AFM images of LNO films are shown in Fig. 2. As seen in Fig. 2a,b the LNO particles consist of clusters of grains with a surface variations of 0–30 nm. The AFM images are consistent with HRSEM pictures (Fig. 1a–c) that showed growth of LNO grains with thickness. The root mean square (rms) roughness of LNO films was found to be 3.1–3.5 nm. The results obtained here are slightly better than by Dong et al. [14] and Li et al. [18] where an rms roughness ranging from 3.78 to 4.67 nm for CSD derived LNO was reported.

The resistivity as a function of thickness was measured for LNO electrodes as shown in Fig. 3. The resistivity reaches a constant value of ~1200 μΩ·cm above a film thickness of 75 nm. Although the grain size increases with thickness, beyond a thickness of 75 nm the grain size does not influence the resistivity. This points out that the LNO resistivity we measure is not influenced by grain boundary effects. Since the grain boundary area in the film is inversely proportional to the square of the grain size, the grain boundary area is reduced by a factor of ~5 between a 75 nm film and 175 nm film in Fig. 3. The lack of sensitivity to this drastic change in grain boundary area indicates that the internal grain resistivity is being measured.

At a thickness of 25 nm, the film consists of discrete grains with "gaps" between them (not shown for lack of space), as evident from the high resistivity shown in Fig. 3. So the nucleation of the grains occurs right at the substrate interface. The second and third layer (up to 75 nm), "fill" the gaps in the film, get it above the percolation limit, beyond which the resistivity becomes constant. Based on the resistivity measurements where the minimal value was obtained at ~75 nm LNO, this electrode thickness (based on three 25 nm deposition cycles) was used for all samples discussed below.

In this work we found that the grain size of the LNO film influences the resulting grain size of the PZT. The morphology of a 200 nm PZT film with 30% PbO excess deposited over LNO with different thickness is presented in Fig. 4. The PZT grains grew from 58 nm to 82 nm as the LNO thickness is increased from 75 nm to 225 nm (Fig. 4a,b). The increase of the LNO grain size by ~50% with its thickness (Fig. 1) gave rise to a ~40% growth of the PZT grains. The average grain size of PZT films (having the same 200 nm PZT thickness) on LNO electrodes is significantly smaller than the PZT grains on Pt electrodes [3] (58 vs. 100 nm [3]). Although the microstructure and grain size of the Pt electrodes is surely different than that of the LNO electrodes, we believe that the marked difference in PZT grain size cannot be explained by the mere morphological differences of the bottom electrode. As will be shown later, the kinetics of PZT crystallization is faster over LNO and the crystallization temperature is lower over LNO when compared to those over Pt. We therefore believe that the considerable decrease of the PZT grain size in PZT/LNO structure compared to the PZT/Pt analog is mainly due to a higher nucleation density on LNO as compared to Pt.

The AFM analysis of PZT/LNO films with 30% PbO excess with smooth and dense surface is shown in Fig. 5. The white spots are foreign dust particles, which are ignored in the roughness analysis. The rms value of PZT film roughness was 1.5 nm which is close to the surface roughness of the underlying LNO electrode. This value is similar to that of Chung et al. [19] where an rms roughness ranging from 1.7 to 3 nm for different Zr/Ti ratio in CSD derived PZT deposited on Pt was reported.

The pure PZT perovskite structure can be obtained only if a precise elemental stoichiometry is kept [20]. Stoichiometry deviations, especially in Pb/(Ti+Zr) ratio, will lead to an undesirable Py phase. The PbO component is usually lost during high temperature processing due to its relatively high vapor pressure and its diffusion into the substrate [1,3]. In order to keep the requested stoichiometry there is a need to compensate the PbO loss by adding excess lead to the precursor. The effect of different PbO excess on the PZT/LNO and PZT/Pt morphology was investigated and discussed below. Fig. 6 shows the morphology of PZT films made with 10% PbO excess on Pt in comparison with PZT on LNO electrodes. In Fig. 6a, two types of grains are observed on the film surface: small grains of ~10 nm and large grains of ~100 nm. Based on our previous work [2], the small grains are ascribed to the Py phase, while large grains are the PZT Perovskite phase. As seen in Fig. 6a, PZT film (with 10% PbO excess) deposited on Pt resulted with more than 50% of the area covered by Py. When PZT was deposited over LNO (under the same conditions) we obtained a drastic decrease in Py content as shown in Fig. 6b. The rate of PZT crystallization in these two cases can be used to explain these
results. It is known that the PZT crystallization rate can strongly influence the Py formation [1]. It was recently found that an increase of the crystallization rate leads to lower PbO loss and therefore decreases the Py content in the final film [3]. Thus, based on the data presented in Fig. 6, it can be concluded that PZT crystallizes faster over LNO than on Pt. Faster crystallization of PZT over LNO is achieved due to rapid nucleation that is the rate limiting step in growth of PZT films [1]. As a result there was a lower PbO loss leading to a much lower Py content in the PZT/LNO system.

Although the Py was drastically decreased in the PZT/LNO system with 10% PbO excess, even a small amount of Py can still significantly deteriorate the ferroelectric properties [3]. Therefore a 30% PbO excess was used in the next steps. No Py grains were observed in either PZT/Pt or PZT/LNO when PZT with 30% of PbO excess was deposited (Fig. 4a,c).

Although, 30% excess of PbO eliminates the formation of Py phase, some nano-pores are observed in the PZT/LNO, as shown in Fig. 4a and Fig. 5. AFM of PZT with 30% PbO excess over LNO; bar-1μm.

Fig. 4. Morphology of 200nm PZT film with 30% PbO excess over of (a) LNO 75nm and (b) LNO 225nm and (c) Pt 100nm; bar-200nm.

Fig. 5. AFM of PZT with 30% PbO excess over LNO; bar-1μm.

We tried long heat treatments at 650 °C for 1 h to see if the natural grain growth at elevated temperatures can eliminate the pores over time. As seen in Fig. 6b, a significant grain growth occurred, but although the number of pores per unit area decreased by pore coarsening (pores merge so that their number decreases but their size increases), they were not eliminated. Therefore, extended annealing time of the PZT film is not sufficient to eliminate these pores. This porosity can be eliminated by using an intermediate level of PbO excess. Experiments with 25% and 20% PbO excess resulted with porous films similar to the 30% PbO case. As shown Fig. 7c, a dense structure without detectable Py phase was obtained with 15% PbO excess. It can be concluded that an optimal PbO excess from the standpoint of dense PZT/LNO morphology is around 15%.

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Fig. 6. Morphology of PZT with 10% PbO excess on (a) Pt and (b) LNO; bar-200nm.

Fig. 7a.
3.2. PZT Crystallization time and temperature

The faster crystallization of PZT films on LNO than on Pt is also observed in a time temperature transformation diagram shown in Fig. 8. It should be noted that the obtained results in Fig. 8 were not influenced by the excess of PbO in the PZT films. Above a temperature of 600 °C, the CSD-derived PZT crystalline phase was obtained after ~10 min over both electrodes. In contrast, at 550 °C PZT still crystallizes over LNO in 10 min, while it takes 45 min to crystallize over Pt electrodes. In addition, PZT can crystallize on LNO at 500 °C in 30 min, while the PZT/Pt system stays amorphous at this temperature, even after an hour. This significant reduction of ~50 °C in the PZT/LNO crystallization temperature relative to PZT/Pt, is consistent with the effective nucleation of PZT grains over LNO. There is a large advantage in the lower annealing temperatures because the undesired diffusion into the substrate and PbO evaporation rates are reduced at lower temperatures. Therefore at lower annealing temperatures a smaller PbO excess in the PZT precursor can be used. Obtaining a dense and crystalline PZT phase at 500 °C, is amongst the lowest reported values for PZT films in general and CSD films in particular. L. Che et al. [21] annealed PZT over LNO for 30 min, but at 600 °C. The lowest reported annealing temperature of PZT is 550 °C for 30 min [19]. In future work, we will concentrate on optimizing the PZT composition and PbO excess at this low temperature.

3.3. Cross sectional morphology and elemental depth profile

The cross sectional view of 400 nm PZT films with 30% of PbO excess, deposited over LNO and Pt electrodes is shown in Fig. 9a and b, respectively. It can be seen that there is no sharp and straight interface between the PZT layer and the LNO electrode (Fig. 9a). This fuzzy interface should be contrasted to the sharp and well defined interface between PZT and Pt shown in Fig. 9b. The strikingly different microstructure shows that a mutual diffusion across the PZT/LNO interface occurs, which is supported by the similar perovskite structure of both PZT and LNO films. This diffusion across the interface region leads to better adhesion and electrical contact between PZT and LNO layers. The ill-defined interface between PZT and LNO also is consistent with the reports of Chae et al [7]. However, it should be pointed that Chae et al [7] have deposited the LNO by magnetron sputtering, whereas in the current work deposition is made by the CSD method. Interestingly, a similar interface structure is obtained in the two different methods.

As seen in Fig. 9a, no significant penetration of Ni, La and O elements into the Si substrate (up to ~20 nm) was observed. The signals indicating a penetration of Ni, La and O about 20 nm into the Si can be ignored due to roughness of the analyzed area that limits the x-axis accuracy.

As seen in Fig. 10b, for the PZT/LNO/Si system, the La and Ni diffuse about 50 nm into the PZT film. In addition, there is a remarkable diffusion of Pb, Zr and Ti across the entire LNO electrode. This data is consistent with the morphology of PZT/LNO cross section (Fig. 9a), where the interface was not well defined. The elemental diffusion can be moderated by lowering the annealing temperature as suggested previously.

3.4. Electrical properties

As discussed above, deposition of 10% excess of PbO in the first layer over Pt electrodes results in formation of Py phase (Fig. 6a). It
was shown that at 10% excess PbO deposited over LNO electrodes gives rise to only a trace amount of Py on the PZT/LNO surface (Fig. 6b). Fig. 11, clearly shows that for 200 nm PZT with 10% excess of PbO the use of LNO bottom electrode increases the fatigue limit (relative to Pt electrode) from $7 \times 10^4$ to $7 \times 10^6$ cycles. One of the reasons of this positive effect is the significant decrease of Py content in PZT film over LNO electrode shown in Fig. 6a,b, consistent with previous findings [3]. The effect of Py can also be observed by comparing the fatigue limits of PZT films with 10% and 30% excess PbO on either Pt or LNO. As shown in Fig. 11, the increase in PbO excess in the PZT/Pt system increases the fatigue limit from $7 \times 10^4$ to $2 \times 10^7$ cycles; whereas the analogous increase in the PZT/LNO system increases the fatigue limit from $6 \times 10^6$ to $7 \times 10^8$ cycles. Finally, the highest fatigue limit of $\sim 1 \times 10^9$ cycles obtained here with 30% excess PbO with the PZT/LNO system, was also found when 15% PbO excess was used. In fact, except for the film porosity (See Fig. 7a,b) and higher number of electrodes with a short circuit, all the other film properties were identical in the 10% and 30% PbO excess films deposited on LNO.

As discussed earlier, Py was not observed (by HRSEM) on the PZT surface after deposition both LNO and Pt electrodes when 30% PbO excess was used. Yet, as seen in Fig. 11, a significant enhancement of the fatigue limit of about two orders of magnitude was found for the PZT/LNO system at 10% of PbO excess and shown in Fig. 12a. It can be noticed that both Ec and Pr values improved in the case of PZT/LNO system. The Ec decreased from 125 kV/cm for PZT/Pt system to 100 kV/cm when LNO was used as bottom electrode. The Pr rose from 25 μC/cm² to 40 μC/cm² for the Pt and LNO electrodes, respectively.

latter mechanism is consistent with the observed diffuse interface of PZT/LNO. It was reported that a fatigue limit of $10^8$–$10^9$ cycles was obtained for PZT/LNO that were made by a CSD method [9,16,24]. Thus the limit of $7 \times 10^8$ cycles obtained here, is amongst the highest to be reported. The only significantly higher fatigue limit we are aware of is $1 \times 10^{11}$ was obtained by Chen et al. [6], however the LNO in that work was deposited by r.f. magnetron sputtering and not CSD.

To evaluate the remnant polarization (Pr) and coercive field (Ec), the ferroelectric hysteresis loops were obtained for PZT/LNO and PZT/Pt at 10% of PbO excess and shown in Fig. 12a. It can be noticed that both Ec and Pr values improved in the case of PZT/LNO system. The Ec decreased from 125 kV/cm for PZT/Pt system to 100 kV/cm when LNO was used as bottom electrode. The Pr rose from 25 μC/cm² to 40 μC/cm² for the Pt and LNO electrodes, respectively.
The decrease in the Ec value with the LNO electrode can be attributed to lower Py content in comparison to Pt electrode as seen in Fig. 6a,b for the 10% excess PbO case. These findings are consistent with previous work [3] where it was shown that the appearance of Py degrades the ferroelectric properties of the film. Furthermore, the decrease in the Ec value can also be related to improved electrical contact [11] between the PZT film and the LNO electrode.

The hysteresis loops of PZT/LNO with 10% and 30% of PbO excess is shown in Fig. 12b. As the PbO content increases from 10% to 30% the Ec decreases from 100 kV/cm to 70 kV/cm (Fig. 12b). The Pr increased from 40 μC/cm² to 50 μC/cm² for the 10% and 30% PbO excess, respectively. It should be mentioned that the ferroelectric properties for PZT/LNO with 15% and 30% of PbO excess were also examined and found to be identical. We have also tested the ferroelectric properties of PZT/Pt with 30% PbO excess. The Ec value was identical to PZT/LNO in the same conditions but the Pr was 40 μC/cm² as compared to 50 μC/cm² in the LNO case.

It should be mentioned that the ferroelectric properties in general, and the Pr values shown in Fig. 12b, in particular, are amongst the best reported results on CSD derived PZT films. These results support the confidence in the CSD method as a viable route to obtain high quality and reliable PZT products.

4. Conclusions

The CSD method was used to prepare both LNO bottom electrodes and overlaying PZT films. The morphology and electrical properties of LNO electrodes were investigated and the influence on structure and ferroelectric properties of PZT/LNO with different PbO excess were investigated in comparison to the PZT/Pt system.

The quantitative dependence of the LNO grain size on the LNO thickness was obtained, where grains grow is proportional to 0.4 power of thickness. A minimal and constant value of the LNO electrode resistivity of ~1200 μΩ·cm was reached at 75 nm thickness, which indicates that the resistivity reflects is not affected by the grain boundary resistance.

The LNO electrode grain size and thickness significantly influences the grain size of the PZT layer: the increase of the LNO grain size by ~50% results in an increase of PZT grain size by ~40%. This effect can be explained by a decrease in the nucleation density of PZT film on larger LNO grains.

The obtained morphology of PZT/Pt system with 10% PbO excess showed that more than 50% of the area covered by Py, in contrast to PZT/LNO system where only a trace of Py was detected, under the same conditions. These results are due to the faster crystallization of PZT over LNO in comparison with PZT/Pt system. No Py grains were observed in both PZT/Pt and PZT/LNO when sol with 30% of PbO excess was deposited, but the PZT/LNO film was found to be porous. Dense structure with no detectable Py phase nor pores was obtained when 15% excess of PbO was used in the PZT/LNO system.

The PZT crystalline phase was obtained in ~10 min above 600 °C regardless of the bottom electrode type. In contrast, at 550 °C PZT crystallized 4 times faster over LNO than over Pt. In addition, crystallization of PZT over LNO was observed to occur at 500 °C whereas the minimal crystallization of PZT was 550 °C. This significant 50 °C reduction in the crystallization temperature is attributed to the higher a effectivity of nucleation of PZT grains over the LNO surface. The lowest annealing temperature that was reported for dense and crystalline PZT films by CSD methods was 500 °C.

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