Surface Composition and Imprint in CSD-Based PZT Films

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Reports on PZT films often suggest the contradicting presence of Pb-deficient pyrochlore (Py) and a Pb-rich layer on the surface. We show that standard Ar⁺ ion sputtering X-ray photoelectron spectroscopy (XPS) depth profiles of PZT films artificially exhibit a Pb-rich surface, independent of actual Pb content of the chemical solution deposition solution. However angle-resolved XPS measurements reveal that films derived from solutions with 10% Pb excess, which give rise to Py surface grains, actually have the expected Pb-deficient surface layer. Alternatively, films derived from solutions with 30% Pb excess are Py free and have Pb-rich surface layer. The Pb-rich films show an increased imprint effect with increasing Pb content.

I. Introduction

In the last two decades there has been much interest in PZT (PbZr,Ti0.52,0.48O3) films due to their special properties and numerous potential applications.1 One of the potentially attractive ways of producing these films is the chemical solution deposition (CSD) method.2 However, this method is still not widely accepted due to insufficient homogeneity of the resulting films on the nano-3,4 and macroscale5 as we have recently described. As a result of these inhomogeneities, the ferroelectric properties are significantly degraded. Specifically, one of the main problems in the Ferroelectric Random Access Memory (FeRAM) applications is an imprint effect, which gives rise to an asymmetric hysteresis loop.6 This effect complicates the design and functioning of FeRAM and reduces its reliability. Currently, there is no explanation for this discrepancy. Moreover, the effect of Pb-rich surface layer on the film properties is not well understood. It was proposed by Watts7,10 that a built-in field can be created at the top interface due to a faster diffusion of Pb⁺⁺ ions to the surface as compared to O²⁻ ions. However, to our best knowledge there are no experimental measurements that correlate the preparation conditions with the Pb inhomogeneity in the films and with the resulting ferroelectric properties.

The main goal of this paper is therefore to study the Pb content in the films in relation to different processing conditions and to correlate the Pb content with the ferroelectric properties. The obtained results are important for understanding the origin of the imprint effect, thus pointing to the processing conditions that avoid it, and improving the PZT films’ performance.

II. Experimental Procedure

The CSD precursors were prepared from the following starting materials: lead acetate trihydrate Pb(OAc)2·3H2O (99.5%, Fluka, Seelze, Germany), titanium iso-propoxide Ti(OCH3)4 (97%, Aldrich, St. Louis, MO) and zirconium acetyl acetonate Zr(OAc)4·H2O (98%, Sigma, St. Louis, MO). The solvent was 1,3-propanediol (99%, Fluka) while acetylacetone (98%, Fluka) was employed as a stabilizer of Ti iso-propoxide. The synthesis procedure was reported in detail previously.8 Precursors were diluted with n-octanol8 and PZT thin films were deposited by spin coating on Pt/Ti/SiO2/Si substrates in class 100 clean room conditions. One cycle consisted of three coatings with intermediate heating for 1 min at 300 °C and final annealing at 650 °C for 10 min. Two series of films were prepared: with 10% and 30% Pb excess. In each series, samples resulting from one, two, and three coating cycles with corresponding film thicknesses of 0.35, ~0.7, and ~1 μm were studied. At least two samples were prepared at similar processing conditions. Gold electrodes with a 500-μm pad diameter were deposited on the films using a
shadow mask technique. The CV characteristics were measured by a Precision Impedance Analyzer, Agilent 4294A (Santa Clara, CA). The applied field for this measurement consisted of a DC bias in the ±10 V range, a scanning time of 5 s, and a low signal oscillator with 50 mV rms and frequency of 1 kHz. The film surface and cross-sectional microstructure were studied with a high-resolution field emission gun (FEG)-equipped scanning electron microscope (LEO 982, Cambridge, U.K.). Conditions included 4-kV accelerating voltage and 3–4-mm working distance, using the in-lens detector of secondary electrons. XPS was used to determine the elemental composition of films. Measurements were carried out with a Thermo VG Scientific Sigma Probe (East Grinstead, U.K.) using a monochromatized AlKα (1486.5 eV) X-ray beam of 400 μm for photoelectron excitation. The spectrometer was calibrated to position the 3d5/2 line of sputter-cleaned Ag at a binding energy of 368.3 eV. A 2 kV rastered Ar⁺ ion beam was used for PZT film sputtering. The Pb4f, Zr3d, Ti2p, and O1s spectra were used for calculation of film composition as a function of depth. Atomic concentration was calculated using a standard bulk PbZr0.5Ti0.5O3 sample (verified with X-ray diffraction) sputtered at the same Ar⁺ ion bombardment conditions. The depth profiles were measured in the standard mode of operation, collecting the photoelectrons at a wide angle of 53±3°, relative to the normal. Etching rate calibration was carried out with a 20-nm SiO2 standard. The angle-resolved measurements did not involve sputtering of the samples (unlike the depth profile). The as-received samples were measured in the bulk- and surface-sensitive modes of operation acquiring the spectra at take-off angles of 30.5±7.5° and 75.5±7.5°, respectively. In the latter experiment, atomic concentration was calculated using a scratched bulk PbZr0.5Ti0.5O3 as a standard. The typical error of the elemental concentration was below 5%. Each measurement except the depth profiles was reproduced on the duplicated samples.

III. Results and Discussion

The typical microstructure of films prepared with 10% and 30% Pb excess is shown in Fig. 1. It can be seen that two types of grains are found on the surface of 10% films in Fig. 1(a): the small grains with ~10-nm diameter above the underlying layer having grains with ~100-nm diameter. The small grains are ascribed to the Py phase while the large grains are the perovskite phase (Per).4,9 As explained in the introduction, the current consensus is that the Py phase forms due to Pb loss during high-temperature processing. The Pb loss ultimately leads to Pb deficiency that is beyond the Per stoichiometry limits and therefore nonstoichiometric Py is formed.9 Because the Pb loss is compensated by 30% Pb excess, no Py grains are observed at any thickness as shown in Figs. 1(b) and (d). We have previously shown9 that the largest Pb loss occurs in the first layer due to lead diffusion into the substrate. Therefore there is a decrease of the Py fraction with increasing film thickness as can be seen when Figs. 1(a) and (c) are compared. By analogy, the lead can accumulate in the 30% Pb excess films with increasing film thickness. After deposition of three layers, particles with a characteristic length of several 100 nm and width of ~10–20 nm are observed on the surface, as highlighted in Fig. 1(d). These particles consistently appear in the 30% films only after deposition of at least three layers and therefore we believe that these particles are formed due to segregation of Pb excess.

Because the goal of this paper is to elucidate whether there is Pb excess or deficiency relative to the stoichiometric Per, we
concentrate on the Pb/(Ti+Zr) atomic ratio. We expected that the sputtering XPS depth profile will reveal the differences in the Pb content between the samples. However, as shown in Fig. 2, there is almost no distinction in the Pb/(Ti+Zr) profile between the various samples, including bulk PZT. Both 10% and 30% films showed decrease in the Pb content as a function of thickness. The results indicate that there is a huge Pb excess up to 700 nm on the surface of each film regardless of the starting composition of the CSD solution. After etching of ~30 nm, the Pb/(Ti+Zr) ratio decreases to unity as expected for stoichiometric Per phase. This result is consistent with the depth profiles elsewhere3,10–15 that show Pb excess on the films surface. However, this result is inconsistent with HRSEM analysis that showed Py particles on the 10% films surface. We associate this contradiction with preferential etching that frequently occurs in Pb containing ceramics.11,13,16 As a result of the preferential etching, the analyzed and actual composition are different. In order to avoid this phenomenon, XPS analysis without etching was performed in the present work.

The depth of XPS analysis decreases with the take-off angle (relative to the normal). Thus, information from deeper parts of the film is measured at smaller take-off angles.16 Therefore two modes of measurement were used: at 30.5° and 75.5° that are characteristic of “bulk” and “surface” compositions, respectively. It should be noted that even measurement in the “bulk” mode characterizes composition of a layer that is thinner than ~10 nm. The region with Pb4f and Zr3d peaks in the “surface” and “bulk” modes of the one-layer PZT film prepared with 10% Pb excess and the three-layer 30% PZT film is shown in Fig. 3. In order to compare the cation ratios in the different measurement modes, the Zr3d peak was normalized in all the spectra. The comparison of “surface” and “bulk” spectra in the 10% Pb excess film clearly shows that the Pb peak is lower in the “surface” mode than in the “bulk” mode. Therefore it can be concluded that this film has a Pb-deficient layer on the surface. This observation is consistent with the Py phase on the surface of this film as was shown in Fig. 1(a). The main difference in the spectrum of 30% Pb excess film is the increase in the Pb signal in both “surface” and “bulk” modes as compared to the 10% film. This is expected since a larger Pb excess was used during film preparation. In addition, the Pb peak in the 30% film is higher in the “surface” mode than in the “bulk” mode. Therefore, unlike the 10% film that showed a Pb-deficient surface, the 30% film shows a Pb-rich surface.

The quantitative Pb/(Ti+Zr) ratios in films prepared with 10% and 30% Pb excess are shown in Fig. 4. The atomic ratios in Fig. 4 were obtained using Pb4f, Zr3d, and Ti2p spectra in different measurement modes and represent an average of the six samples in each case. The measurements do not involve etching of the samples (unlike the depth profile measurement). The difference between the surface and bulk modes are in the take-off angle of 30.5° ± 7.5° and 75.5° ± 7.5°, respectively, in which the data are collected. The dashed line in Fig. 4 represents an ideal Per phase where the ratio of Pb/(Ti+Zr) equals unity. The Pb/(Ti+Zr) ratio indicates the phase content on the surface: PbO segregation in indicated by a ratio > 1, while a significant amount of Py is indicated by a ratio < 1. It can be seen that in contrast to the sputtering XPS experiment, there is a significant difference between the films prepared with 10% and 30% of Pb excess in angle resolved measurement. The Pb/(Ti+Zr) ratio in 10% films with surface Py is below unity indicating Pb deficiency, while 30% films show Pb excess. In the films with 10% Pb excess, the average “bulk” ratio is consistently higher than the “surface” ratio. This effect is reversed in the films with 30% Pb excess. Thus we can conclude that the surface of the 10% films is Pb deficient while the surface of the 30% films is Pb rich. It can be noted from Fig. 2 that the asymptotic cation ratio in all films is unity, indicating that the nonstoichiometry is limited to the surface layer. It should be emphasized that the difference of the Pb/(Ti+Zr) atomic ratio at 0-nm depth in Fig. 2 and in the “surface” mode in Fig. 4 is due to the preferential lead etching in the depth profile case, which gives rise to an apparently high and incorrect Pb content on the top 40 nm.

The average Pb/(Ti+Zr) ratio on the surface of the 10% film is 0.8. The Per phase is not stable at this nonstoichiometry9 and therefore the Py phase is expected on the surface of these films. This is consistent with the Py particles in the 10% films shown in Figs 1(a) and (c). The average Pb/(Ti+Zr) ratio of 1.7 on the surface of the 30% film is also beyond the Per stability limits. Thus, segregation of PbO is expected in these films, which correlates with the appearance of the particles on the surface of the three-layer-thick film with 30% Pb excess in Fig. 1(d).

The CV characteristics of the films prepared with 10% and 30% Pb excess are presented in Fig. 5. It can be seen that in both cases the dielectric constant increases with thickness, consistent with previous results.4 The 10% film, Fig. 5(a), showed symmetric CV curves, as usually observed for classical ferroelectric films.5 However, the 30% films, Fig. 5(b), exhibited a shift of the
curves’ intersection point to a negative bias as shown by a dashed arrow. This effect can be explained by a permanent dipole that is “imprinted” into the surface region due to the higher mobility of the Pb$^{2+}$ ions to the surface relative to that of the O$^{2-}$ ions as originally suggested by Watts et al.7 The “imprinted” dipole causes the shift of the signal in the observed direction because the domains in these films switch more easily when a positive bias is applied. The results were well reproducible with repetitive measurements of the fresh samples as well as on samples that we stored for 1–2 months.

It is interesting that the negative shift increases with layer number in the case of 30% films. This is another evidence of Pb excess accumulation that increases with each layer, consistent with the HRSEM image in Fig. 1(d). The presence of excess lead is consistent with our previous results that showed a decreased grain size in 30% films as compared with the 10% films, due to inhibition of grain growth in these films by the excess PbO.4 Thus it can be concluded that as a result of Pb accumulation in the film the imprint effect is amplified. On the other hand, 30/10/10 films with 30% Pb excess in the first layer (to compensate for the higher Pb loss into the substrate) and 10% in the following layers4 showed similar CV characteristics (no imprint effect) and grain size6 to the 10% films, indicating that there was no Pb accumulation in this case.

IV. Summary

This paper suggests that the surface of the sol–gel-derived PZT films is not always Pb rich as often reported in the literature.5,10–15 Preferential etching during depth profile measurement appears to mask the distinction between the surfaces with different compositions, while angle-resolved XPS measurements enable a distinction between them. The presence of the Py grains on the surface is accompanied with the Pb/(Ti+Zr) ratio below one. On the other hand, the Py-free films prepared with 30% Pb excess showed a Pb/(Ti+Zr) ratio above one indicating Pb segregation on the surface. The CV characteristics showed symmetric curves in 10% films while curves of 30% films were highly asymmetric due to an imprint effect. The curves intersection shifted to the negative bias in the 30% films, indicating a positive built-in field in the film. This effect can be explained by the faster diffusion to the film surface of Pb$^{2+}$ compared with O$^{2-}$ ions, as was previously suggested by Watts.7 Following the CV pattern of the film allows fine-tuning of the Pb surface content. This allows avoiding imprint effect and therefore improves the quality of PZT films in FeRAM and other industrial applications.

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References