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Mixed titania-lead oxide seed layers for PZT growth on Pt(111): a study on nucleation, texture and properties

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Abstract

Growth and properties of sputter in situ sputter deposited $Pb(Z,Ti)O_3$ (PZT) thin films have been studied on (111)-textured Pt electrodes as a function of seed layers of the type $(TiO_2)_x(PbO)_y$. The PZT process was run with a limited lead excess resulting in pyrochlore nucleation on bare Pt electrodes. When the electrode was covered with a dense seed layer, perovskite was obtained everywhere. Ti rich seed layers yielded (111)-textured PZT even for very thin seed layers. Pb rich seed layers nucleated as $PbTiO_3\{100\}$ and gave rise to (100)-textured PZT. In an intermediate zone, the major perovskite orientations (100), (110) and (111) have been found together with pyrochlore for a small seed layer thickness. In this zone, the seed layer nucleates in islands leaving bare Pt spots. The intermediate region is a transition region between (111) seeds and (100) seeds. The latter exhibit diverging critical sizes at a given critical flux ratio, leading to large nuclei and bare Pt.

Keywords: Dielectric properties; Films; Interfaces; Perovskites; PZT

1. Introduction

The perovskite material $Pb(Zr,Ti)O_3$ is sufficiently complex to exhibit a nucleation controlled growth, as observed in the early days of sol-gel process development.[1] With suitable substrates, the activation energy for nucleation can therefore be reduced. It was for instance shown that the growth temperature of PZT can be reduced using $PbTiO_3$ template layers.[2] Quite a number of atoms have to be gathered correctly to define a nucleus of a given orientation. When a film is grown in situ, or nucleation is stimulated by the substrate, the first atoms involved in nucleation are those on the substrate. It is evident that low index planes are defined by less atoms, and thus form more easily as their correct gathering is more likely.[3] For this reason, thin film grains generally exhibit a low index plane orientation with respect to the substrate, even on non-ordered or differently ordered surfaces. In case of PZT one usually observes (100), (110) or (111) orientation. It is of interest to grow textured films, because properties are generally optimal at a given orientation only. A good starting point for textured PZT growth is a well textured Pt(111) electrode. Although geometry and atom distance on this trigonal surface correspond not too badly to PZT(111), PZT(111) nucleates not much better than PZT(100) on this surface. With sol-gel processing, the resulting texture is much dependent on lead excess, pyrolysis temperature and ramping speed during the crystallization anneal.[4] Better results are obtained by adding a seeding layer that lowers the nucleation activation energy for a certain orientation only. It was shown that thin layers of $PbTiO_3$ can be obtained in $\{100\}$ orientation on (111)-textured Pt electrode films by means of in situ sputter deposition, and that such layers pass their orientation to PZT grown on top of them.[5,6] Very helpful to achieve (111) films are thin (1–3 nm) TiO_2 seeding layers on top of Pt(111).[7,8] In this work we investigate the complete range of seeding layers nominally consisting of $(TiO_2)_x(PbO)_y$, addressing the morphology and phase of the seeding layers, the orientation and phase they pass to the PZT grown on top of them, and their effect on the dielectric constant of PZT.

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2. Experimental

A schematic of the layer sequence is drawn in Fig. 1. The bulk substrate consists of thermally oxidized silicon wafers. Pt(111) electrodes have been sputter deposited using TiO_2/Ti adhesion layers. The $(TiO_2)_x(PbO)_y$ seeding layer has been sputter deposited at 530 °C from two sputter sources (dynamic sputtering). Since the amount of PbO desorption is not known, we classified the seeding layers according to the TiO_2 film thickness in absence of PbO flux, and the applied PbO flux in fractions of the total flux of PbO and TiO_2. PZT45/55 was afterwards in situ sputter deposited from three metallic targets in a dynamic sputtering mode at 580 °C (see Ref. 8 for more details). The lead flux was chosen as 0.69 of the total flux of the metal-oxides. Such conditions yielded pyrochlore on unseeded films, and perovskite on well seeded films.

3. Results and discussion

The obtained films were analysed by means of θ–2θ X-ray diffraction (XRD) and scanning electrode Microscopy (SEM). Figs. 2 and 3 display some SEM pictures of the obtained results. In case of thick seed layers, the orientation varies from (111) over random to (100) with increasing lead flux. When the seed layer is very thin, pyrochlore is mainly formed in an intermediate compositional range with lead excess. The results are compiled in a diagram (see Fig. 4). Two regions with pure (111) and (100) phases can be clearly distinguished. They are separated by a relatively narrow region around a lead flux of 0.7 where random growth occurs, including (110) orientation. In this zone, pyrochlore is growing as well, especially at thin seeding layers. The following mechanisms explain the phase diagram: thin TiO_2 films—even when including some PbO—cover completely the Pt surface[7] and allow a dense nucleation of PZT(111). There is no PbO desorption, all the PbO reacts with TiO_2. At PbO = 0.5, the seed layer transforms to PT(111) grains that are densely nucleated and yield as well PZT(111) (not shown in this article). Around a PbO flux of 0.7, the seed layer starts nucleating in (100), (110) and (111) orientation. Larger nuclei with a lower density are formed, leaving bare Pt in between. The open Pt leads to pyrochlore formation. The fraction of bare Pt has been assessed by Auger Electron Spectroscopy (AES) (see Fig. 5). Only the topmost atoms contribute to the signal. The Pt signal corresponds thus fairly well to the area of uncovered Pt. Fig. 5 shows that pyrochlore formation is closely related to uncovered Pt. It is necessary to cover more than 85% of Pt to avoid pyrochlore formation. The desorption on bare Pt must be quite important. For nucleation of PT(100) (possibly also of PT(110)) the PbO pressure plays the role of the supersaturation parameter. The pyrochlore spike in the phase diagram can be understood as the divergence of nucleus size when approaching the critical PbO pressure. It is thought that an excess of PbO is needed during nucleation of PT(100) in order to achieve a low surface energy with PbO terminated nuclei.[7] For this reason, and also because of lead oxide desorption on bare Pt, the critical region between (100) and (111) orientation is on the PbO rich side of the diagram.

We investigated as well the impact of such seed layer on properties. One may argue that $PbTiO_3$ seed layers may lower the dielectric constant of PZT. A series of depositions has been performed where the seed layer thickness and the PbO flux during seed layer deposition

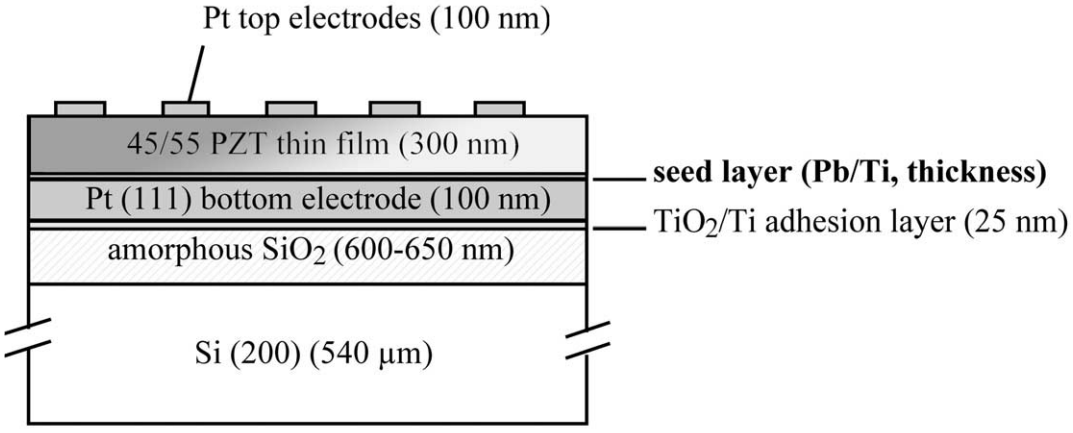

Fig. 1. Schematic drawing of the deposited layer sequence.

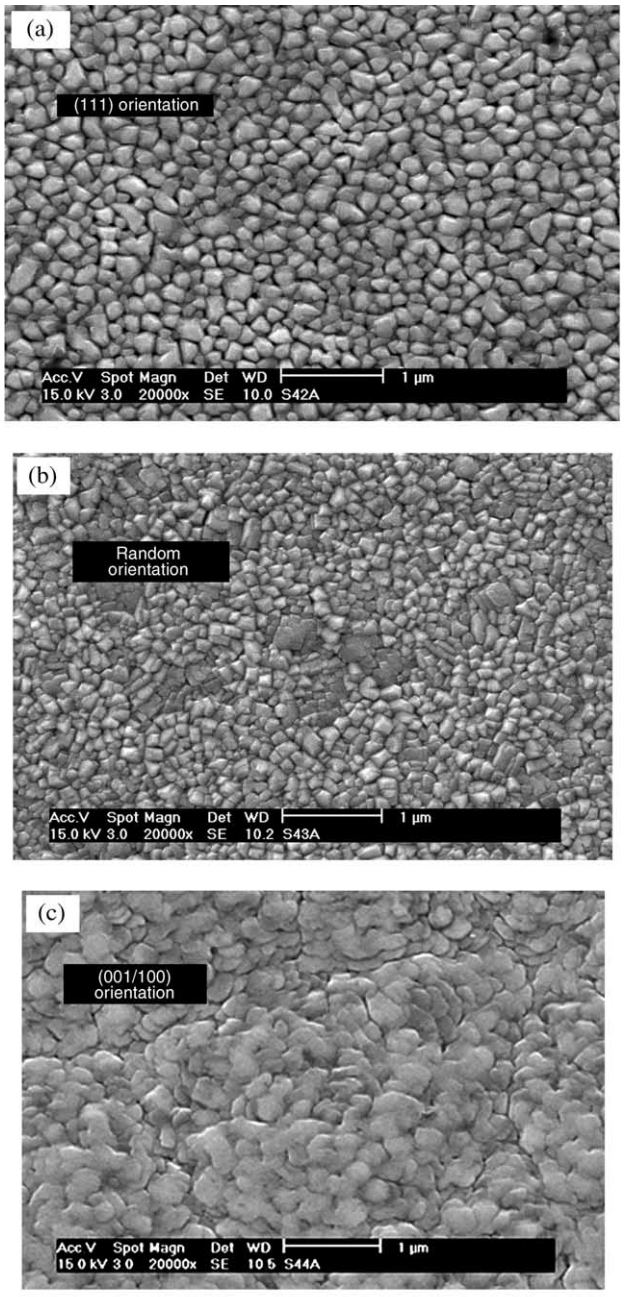

Fig. 2. SEM micrographs of PZT 5/55 films deposited on Pt(111) seeded with 10 nm thick equivalent TiO_2 layer and with relative PbO flux of (a) 0.55, (b) 0.69, (c) 0.77. The following textures have been observed by XRD: (a) (111), (b) random, and (c) {100}.

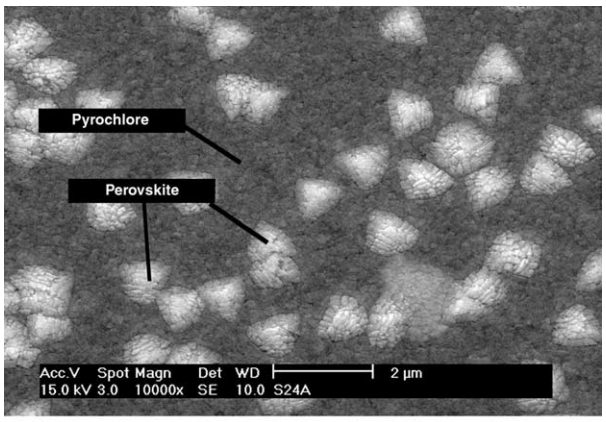

Fig. 3. SEM micrograph of film deposited on Pt (111) with 1.5 nm thick equivalent TiO_2 seed layer and with a PbO/TiO_2 flux ratio of 0.77. Perovskite grains are embedded in a pyrochlore matrix.

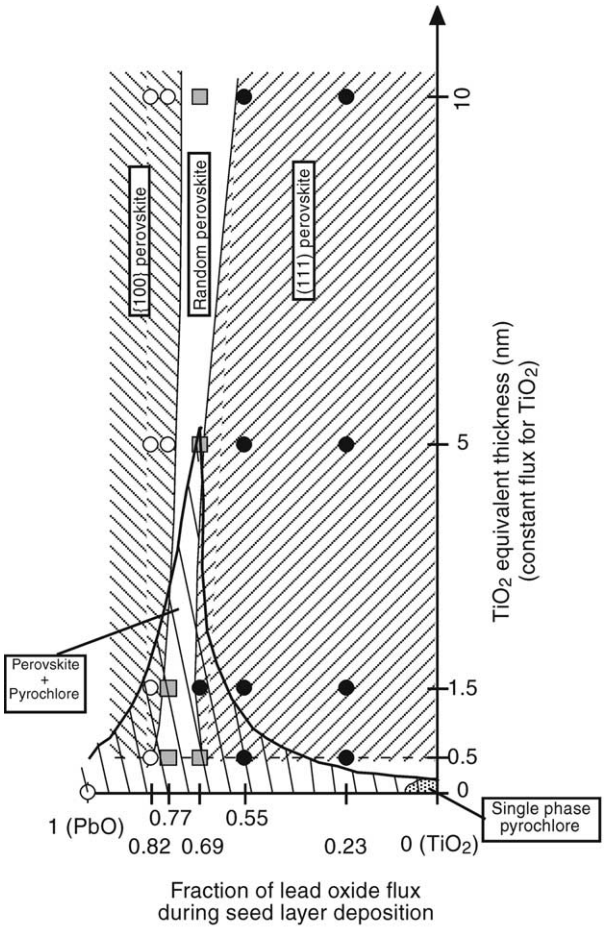

Fig. 4. Diagram summarizing PZT texture and presence of pyrochlore as a function of seed layer composition and thickness.

was varied. In order to avoid ambiguities due to changing film orientations, we chose to grow first a TiO_2 seed layer that warranties (111)-orientation for all cases. The result is shown in Fig. 6. It shows that thick seed layers indeed decrease the dielectric constant as expected. However, thin seed layers improve the dielectric constant, especially if they are deposited with large lead fluxes. We could show that the lattice dielectric constant is the same for all films of a given seed layer thickness. What improves with increasing lead flux is the domain wall contribution.

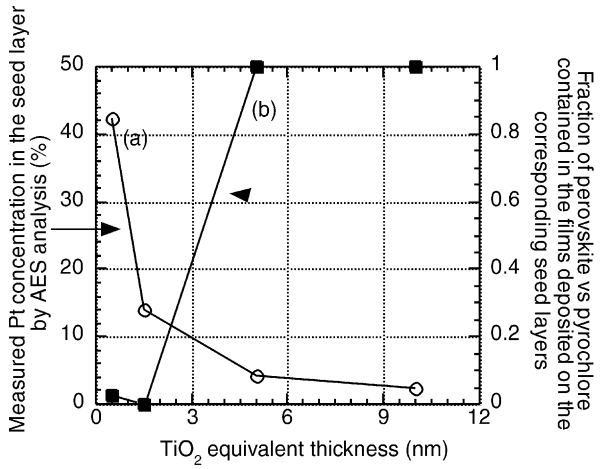

Fig. 5. Pt concentrations in the seed layers deposited at constant fraction of PbO flux (0.77) measured by AES analysis and (b) fraction of perovskite versus pyrochlore contained in the films deposited on the corresponding seed layers, as a function of the TiO_2 equivalent thickness.

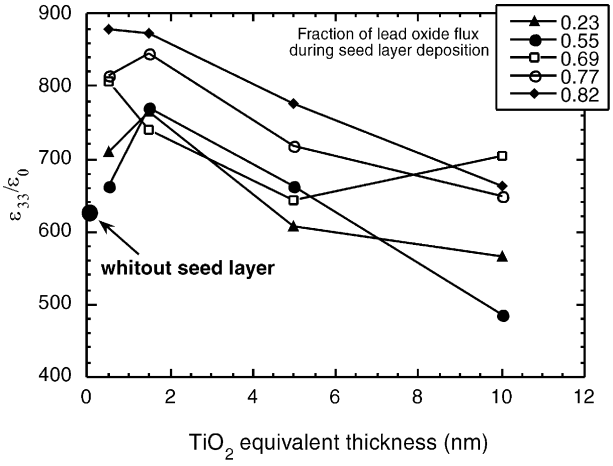

Fig. 6. Initial relative permittivities of the deposited films as a function of equivalent TiO_2 thicknesses and fraction of PbO fluxes during the deposition of the seed layer.

4. Conclusions

The seeding of PZT thin films with few nm thick $(TiO_2)_x(PbO)_y$ layers has been investigated. Pure (111) and (100) orientations have been obtained, whereas the (110) orientation occurs in mixed or random orientations only. Ti-rich seed layers yield (111) orientation and Pb-rich seed layers yield (100) orientation. In the latter case, the seed layer consists of $PbTiO_3\{100\}$. A roughening of the seed layer occurs in the intermediate region due to nucleation of (100) and (110) seeds at critical lead fluxes. Bare platinum appears between nuclei giving rise to pyrochlore formation.

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