

Electrical properties and leakage current behavior of un-doped and Ti-doped lead zirconate thin films synthesized by sol–gel method

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Abstract

Un-doped and Ti-doped (5, 10 and 15 mol%) antiferroelectric and ferroelectric lead zirconate–PbZrO₃ (PZ) thin films were prepared by sol–gel spin coating method. All PZ films crystallized in the perovskite phase with full [111] pseudocubic orientation with a uniform microstructure. The paraelectric–ferroelectric phase transition temperature was found to shift to lower values and the electrical properties were found to degrade as a result of decreasing film thickness. The leakage current of the un-doped PZ films were dominated by the space-charge-limited current, whereas Poole–Frenkel conduction mechanism was found to be dominant at the Ti-doped films at high electric fields.

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1. Introduction

Antiferroelectric (AFE) thin films are promising materials for various applications such as high-energy density storage capacitors and digital actuators in microelectromechanical (MEMS) systems [1–3]. The antiferroelectric phase can be switched spontaneously into a ferroelectric phase by application of a sufficient electric field [4]. Antiferroelectrics have spontaneous polarization that is aligned along the same direction in the same column and in the opposite direction in the neighboring columns; therefore it exhibits no net polarization. Due to the field induced AFE to ferroelectric (FE) phase transition they release the stored charge at a certain voltage when the field is removed.

The typical and one of the most widely studied antiferroelectric composition is the lead zirconate–PbZrO₃ (PZ). It crystallizes in the perovskite structure with an orthorhombic super lattice structure. When composition of PbZrO₃ is modified into Pb(Zr_{1-x}Ti_x)O₃, a structural change occurs at $x \approx 0.075$ from orthorhombic antiferroelectric into a rhombohedral ferroelectric

phase. Various Zr/Ti ratios have been investigated in the PbZrO₃–PbTiO₃ binary phase diagram and most of the studies were focused on the morphotropic phase boundary composition or in the Ti-rich region of the PZ-PT system. Whereas, there are relatively fewer studies in the literature on the AFE region compared to the FE one [5].

Our previous studies [6–8] on PZ thin films were focused on the synthesis of the films by sol–gel method and investigation of the structure-property relationships in these films. However, considering the intended applications of these films in high energy density storage and decoupling capacitors on multichip modules, the leakage current gains an utmost importance [9].

In this article, we report on the dielectric and polarization vs. electric field (P–E) hysteresis properties of sol–gel derived un-doped and Ti-doped antiferroelectric and ferroelectric PZ thin films. A special emphasis was given on analysis of the leakage current behavior of the thin film capacitors.

2. Experimental procedure

Un-doped and Ti-doped PZ films were obtained by sol–gel spin coating process. The PZ solutions were prepared with 10 mol% Pb excess. Lead acetate trihydrate [Pb(CH₃COO)₂·3H₂O] and zirconium n-butoxide n-butanol [Zr(O(CH₂)₃CH₃)₄·CH₃(CH₂)₃OH]

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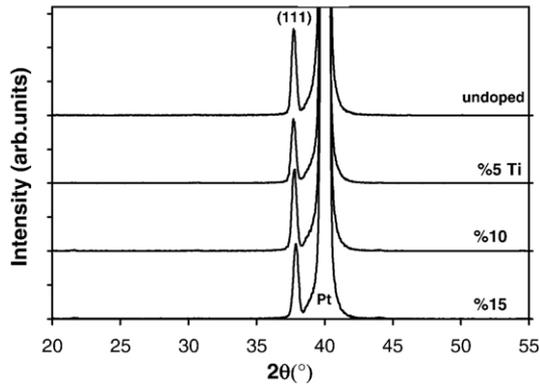


Fig. 1. X-ray diffraction patterns of un-doped and Ti-doped PbZrO_3 thin films.

were the starting materials to prepare PZ solution. They were dissolved separately in 2-methoxyethanol ($\text{C}_3\text{H}_8\text{O}_2$) at 80°C for 30 min. These two solutions were dehydrated at 120°C for 90 min. The final lead zirconate precursor solutions were then obtained by mixing Pb and Zr solutions at 80°C for 30 min followed by a final dehydration step at 120°C for 90 min. These PZ precursor solutions were prepared with 0.4 M concentration. On the other hand, titanium tetraisopropoxide was used as a titanium source to prepare the Ti-doped PZ films. Ti-doped PZ precursor solution was prepared by the addition of 5%, 10% and 15 mol% Ti source into the PZ precursor solution at the final mixing step.

Prior to coating the films, the precursor solutions were aged for 24 hours. The deposition of all the PZ thin films on $\text{Pt}_{(111)}/\text{Ti}/\text{SiO}_2/\text{Si}_{(100)}$ substrates was performed by sol–gel spin-coating method using the following settings of 600 rpm for 6 s and 3000 rpm for 60 s. The drying step was performed at 150°C for 5 min and the pyrolysis was done at 400°C for 5 min. These steps were repeated until obtaining PZ films with the desired thickness. In this study, PZ films were produced between 100 and 400 nm thickness. Finally, the films were sintered under atmospheric conditions at 700°C for 60 min to reach the final crystallization. In order to evaluate the electrical properties of these films 200 nm-thick platinum top electrodes with 100, 200 and 400 μm diameter were deposited on the surface of the films by radio frequency magnetron sputtering method using a shadow mask.

The crystallographic structure of PZ thin films was investigated using a Philips X-pert X-ray diffractometer (XRD) with $\text{Cu K}\alpha$ radiation. The chemical composition was confirmed using Philips MagiX X-ray fluorescence spectroscopy (XRF). Microstructural properties of the films were examined using a Jeol JSM-6301F field emission scanning electron microscope (SEM). Electrical properties of the PZ films were measured using AixACCT TF Analyzer 2000 and Radiant RT6000 ferroelectric testers.

3. Results and discussion

3.1. Phase analysis

Fig. 1 shows the XRD pattern of 200 nm-thick un-doped and Ti-doped PZ films on $\text{Pt}/\text{Ti}/\text{SiO}_2/\text{Si}$ substrates. All of these films

were obtained under identical processing conditions. Fig. 1 clearly indicates that all the PZ films crystallized in the perovskite phase with full $[111]_{\text{pc}}$ orientation. A secondary phase has not been observed in any of the films. Crystallographic orientation and microstructural homogeneity in PZ thin films are closely related to the processing conditions. The electrical properties, in turn, are severely affected from the orientation and the microstructural features of the films. From our earlier studies [6] on un-doped, as well as Ce, Er and Cr-doped PZ films, we found that applying a single pyrolysis step at 300°C followed by annealing at 600 – 800°C for 10 min after coating each PZ layer resulted in a randomly oriented thin film with a heterogeneous two-phase microstructure. However, it was also determined that these structural features have an adverse effect on the electrical properties. After that first study, it was decided that the processing conditions of the films have a critical role on the microstructure and especially electrical features of the films and they, therefore, have to be modified in order to obtain PZ films with better properties. In a follow-up study [7], using a two step pyrolysis process with a lower drying temperature (150°C), and a single annealing step at the end of coating desired thickness were found to yield $[111]_{\text{pc}}$ orientation and a uniform microstructure with superior electrical properties. A discussion and explanation of the relationship between the processing conditions and film orientation have been presented elsewhere [7]. Films with $[111]_{\text{pc}}$ orientation were determined to have superior electrical properties [8]. Based on these prior results, the un-doped and Ti-doped PZ films in the present study were prepared under experimental conditions that would yield full $[111]_{\text{pc}}$ orientation and a uniform microstructure.

From Fig. 1, although un-doped and 5%, 10% or 15% Ti-doped films have full $[111]_{\text{pc}}$ orientation, the 2θ angle of the (111) diffraction peak shifts to higher angles as a function of increasing Ti content. According to Bragg equation ($n\lambda = 2d_{\text{hkl}}\sin\theta$), this shift indicates a decrease in the d_{111} interatomic layer spacing and, therefore, a decrease in the unit cell dimensions, as shown in Fig. 2. This decrease is consistent with the literature on lead zirconate in both bulk [10,11] and in thin film form [12] and can be justified by the smaller size of the

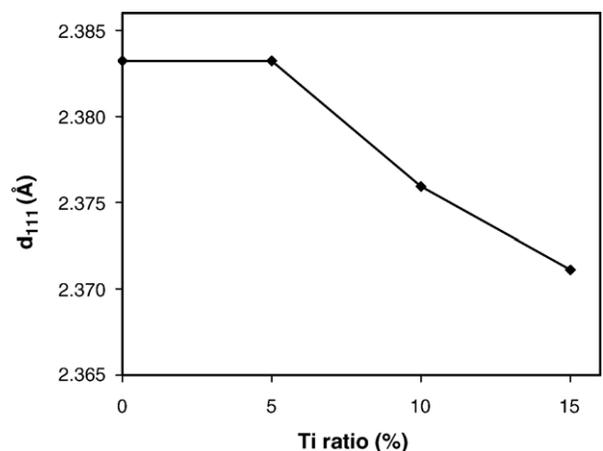


Fig. 2. Variation of the spacing of the d_{111} interatomic layers as a function of increased titanium content.

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